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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 25°.¹

BY H. N. MORSE AND W. W. HOLLAND.

Having improved our methods of work² to a point where we feel confident of the correctness of our results to the second decimal place of the numbers expressing the osmotic pressures,³ we determined to make a serious attempt to ascertain the temperature coefficient of the force. With this in view, it was decided to measure the pressures of cane sugar solutions, ranging in concentration from 0.1 to 1.0 *weight-normal*, at intervals of five degrees, from 0° to 30°. The earliest measurements (Series I.⁴ and II.⁵) were discarded, because they were made while the method was still in a somewhat crude state and liable to yield results in which the errors might equal, or even exceed, any probable temperature coefficient. Series III.⁶ and IV.,⁷

¹ The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon this subject will be found in *THIS JOURNAL*, 26, 80; 28, 1; 29, 173; 32, 93; 34, 1; 35, 1 and 39; 37, 324, 425, and 558; 38, 175; 39, 667; 40, 1, 194, 266, and 325.

² *THIS JOURNAL*, 40, 266 and 325.

³ *Ibid.*, 40, 4.

⁴ *Ibid.*, 34, 1.

⁵ *Ibid.*, 36, 39.

⁶ *Ibid.*, 37, 425.

⁷ *Ibid.*, 38, 175.

on the other hand, the former at 0° and the latter at temperatures between 4° and 5° , were carried out after some of the larger defects of the method had been remedied; and they have, on that account, been temporarily retained for purposes of comparison.¹ But these also will soon disappear from any discussion of the temperature coefficient of osmotic pressure, if we succeed, as we expect during the coming winter, in carrying through new series of measurements at precisely 0° and 5° . The proposed work at 10° and 15° has already been published.² The measurements at 25° are given in the present paper, while those at 20° and 30° are already under way.

The results which were obtained at 25° are presented in this paper in the customary form, in a series of twenty-two tables. Tables I. to XX. contain the data pertaining to each of the duplicate determinations of the pressure of the usual ten concentrations of solution. Table XXI. gives a summary of the results of each experiment, while Table XXII. presents the mean values of these results for each concentration.

An explanation of our methods of recording and of calculation may serve to forestall a possible criticism of some of the figures which appear in the tables. It will be noticed in Tables I. and II. that the rotation, in one case, is recorded as $12^{\circ}.6$, and in the other as $12^{\circ}.8$. The difference, $0^{\circ}.2$, is due, not to differences in the ratios of water to sugar molecules, but mainly to the fact that the temperatures of the two solutions differed by nearly 9° , the temperature of one solution being $28^{\circ}.5$, and of the other $19^{\circ}.8$. In a minor degree it is due to the fact that we do not attempt to read the polarimeter closer than $0^{\circ}.05$, so that a rotation of $0^{\circ}.08$ would be recorded as $0^{\circ}.1$, and one of $0^{\circ}.18$ as $0^{\circ}.2$, while rotations of $0^{\circ}.02$ and $0^{\circ}.13$ would be recorded as $0^{\circ}.00$ and $0^{\circ}.15$, etc. We do not endeavor to determine the rotation of the solutions at the precise temperature at which the osmotic pressure is measured, since, for our purpose—the detection of loss in concentration while in the cell—it is only necessary that the two solutions which are compared, namely, the original one and that removed

¹ THIS JOURNAL, 40, 208.

² *Ibid.*, 39, 667; 40, 194.

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from the cell after an experiment, shall be at the *same* temperature at the time of the polariscopic examination. Again, it will be noted that only one pressure of the atmosphere is given for each experiment. This is the *mean* pressure of the atmosphere during the whole time of the experiment. Each individual observation of osmotic pressure is corrected, of course, for the exact atmospheric pressure which prevailed at the time of reading the manometer. Any apparent slight discrepancies between the recorded volumes of the nitrogen in the manometer and the corresponding osmotic pressures are due to the practice of recording only to the second place of decimals, while in the actual computations, decimals in the third and fourth places are taken into account in order to calculate a little more precisely the mean osmotic pressure, the ratio of osmotic to gas pressure, etc. The practice, however, sometimes leads to discrepancies in the records which appear at first sight to be errors in arithmetic. An example of this will be found in Tables I. and II., where the recorded osmotic pressures are identical, 2.56 atmospheres, as are also the gas pressures, 2.43 atmospheres; and yet the ratio of osmotic to gas pressure in one case is 1.055, and in the other 1.051. For the reassurance of those who may have been disturbed by any seeming inconsistencies in the records such as have been pointed out, we wish to say that unusual care is taken to avoid errors in computation. In most cases, the results have been calculated independently by two individuals, and have then been revised by a third; and if any real errors have crept into the records, they have eluded the vigilance of not less than two computers.

In the first twelve of the twenty determinations of pressure at 25° (see Table XXI.), while the solutions were in the cells, there was no loss in concentration which could be detected by the polariscope. In this list are included the pressures of concentrations 0.1 to 0.6, inclusive. In seven of the eight remaining experiments, there was a slight loss in rotation, which, however, was small in comparison with the pressures measured. We have given in former papers our reasons for regarding this loss as due principally to a dilution of the cell contents which occurs *subsequent* to the measurement of pres-

sure, and which is, therefore, without effect upon the accuracy of the experiment. Accordingly, no correction for dilution has been applied in calculating the osmotic pressures which are recorded in the tables. Nevertheless, we have given, in each case where a loss in rotation was observed, the correction which would be applied if the loss were regarded as due to inversion. The maximum correction for any one concentration (the normal solution, see Table XX.) was 0.03 atmosphere in a total pressure of 26.33 atmospheres, which would not materially affect the ratio of osmotic to gas pressure.

Throughout the work, the temperature of the solutions did not deviate sensibly from 25°, while the temperature of the space occupied by the manometers differed only slightly from that of the solutions. The "*thermometer effects*" cannot, therefore, have been serious. However, we do not flatter ourselves that *thermometer effects* have been wholly eliminated, for the slight fluctuations which are observed after the pressure has reached a maximum we still believe to be due, as a rule, to small changes in the temperature of the solutions. The osmotic cell is also an extremely sensitive thermometer, and it is easily possible for it to indicate changes of temperature which would not be detected by the ordinary mercury thermometer, which is graduated in tenths of a degree.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 12°.6; (2) at conclusion of expr., 12°.6; loss, 0. *Manometer*: No. 13; volume of nitrogen, 432.33; displacement, 0.04 mm. Cell used, C₃. Resistance of membrane, 143,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.46; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.49. Time of setting up cell, 4.00 P. M., June 18, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 18.						
11.00 P.M.	25°.00	25°.00	140.31	2.56	2.43	0.13
June 19.						
10.00 A.M.	25°.00	24°.90	139.26	2.57	"	0.14
10.00 P.M.	25°.00	25°.10	140.42	2.56	"	0.13
June 20.						
10.30 P.M.	25°.00	25°.10	140.32	2.56	"	0.13
				2.56	2.43	0.13

Molecular osmotic pressure, 25.63.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.055.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, 12°.8; (2) at conclusion of expr., 12°.8; loss, 0. *Manometer*: No. 20; volume of nitrogen, 415.91; displacement, 0. Cell used, B₃. Resistance of membrane, 225,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.42; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.12. Time of setting up cell, 5.00 P. M., Oct. 27, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 29.						
9.00 A.M.	25°.00	24°.90	133.62	2.55	2.43	0.12
4.30 P.M.	25°.00	24°.90	133.55	2.56	"	0.13
10.00 P.M.	25°.00	25°.00	133.51	2.56	"	0.13
Oct. 30.						
12.00 M.	25°.00	24°.95	133.30	2.55	"	0.12
				2.56	2.43	0.13

Molecular osmotic pressure, 25.55.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.051.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $24^{\circ}.95$; (2) at conclusion of expr., $24^{\circ}.95$; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, G. Resistance of membrane, 550,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.55; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.68. Time of setting up cell, 5.00 P. M., Oct. 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 26.						
1.00 P.M.	25°.00	25°.10	85.57	5.08	4.86	0.22
5.00 P.M.	25°.00	25°.00	85.65	5.07	"	0.21
8.00 P.M.	25°.00	25°.00	85.24	5.10	"	0.24
Oct. 27.						
8.00 A.M.	25°.00	25°.00	85.21	5.09	"	0.23
				5.09	4.86	0.23

Molecular osmotic pressure, 25.43.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.046.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original $24^{\circ}.95$; (2) at conclusion of expr., $24^{\circ}.95$; loss, 0. *Manometer*: No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, D. Resistance of membrane, 550,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.47; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.86. Time of setting up cell, 5.00 P.M., Oct. 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 25.						
9.30 A.M.	25°.00	24°.95	67.81	5.10	4.86	0.24
12.30 P.M.	25°.00	25°.00	67.77	5.10	"	0.24
9.00 P.M.	25°.00	25°.00	67.57	5.11	"	0.25
Oct. 26.						
1.00 P.M.	25°.00	25°.00	68.08	5.08	"	0.22
				5.10	4.86	0.24

Molecular osmotic pressure, 25.49.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.049.

Table V.

0.3 Wt. normal solution. Exp. No. 1. Rotation: (1) original, $36^{\circ}.6$; (2) at conclusion of expr., $36^{\circ}.6$; loss, 0. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.06 mm. Cell used, B₃. Resistance of membrane, 190,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.44. Time of setting up cell, 4.00 P. M., June 30, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
July 1.						
10.00 A.M.	25°.00	25°.30	54.03	7.58	7.29	0.29
1.00 P.M.	25°.00	25°.40	54.05	7.57	"	0.28
11.00 P.M.	25°.00	25°.50	54.04	7.57	"	0.28
July 2.						
10.30 A.M.	25°.00	25°.10	54.01	7.58	"	0.29
				7.58	7.29	0.29

Molecular osmotic pressure, 25.27.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.040.

Table VI.

0.3 Wt. normal solution. Exp. No. 2. Rotation: (1) original, $36^{\circ}.7$; (2) at conclusion of expr., $36^{\circ}.7$; loss, 0. *Manometer*: No. 13; volume of nitrogen, 432.33; displacement, 0.00. Cell used, B₃. Resistance of membrane, 275,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.35. Time of setting up cell, 4.00 P. M., Oct. 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Oct. 25.						
9.30 A.M.	25°.00	24°.95	54.33	7.55	7.29	0.26
4.00 P.M.	25°.00	25°.00	54.24	7.56	"	0.27
10.00 P.M.	25°.00	25°.00	54.34	7.55	"	0.26
Oct. 26.						
9.00 A.M.	25°.00	25°.00	54.47	7.54	"	0.25
				7.55	7.29	0.26

Molecular osmotic pressure, 25.17.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.036.

Table VII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original $47^{\circ}.9$; (2) at conclusion of expr., $47^{\circ}.9$; loss, 0. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, B₃. Resistance of membrane, 104,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.14. Time of setting up cell, 5.00 P. M., May 29, 1908.

Time. May 30.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
9.00 A.M.	25°.00	25°.00	38.73	10.10	9.72	0.38
12.00 M.	25°.00	25°.10	38.71	10.10	"	0.38
4.00 P.M.	25°.00	25°.10	38.78	10.09	"	0.37
12.00 P.M.	25°.00	25°.20	38.76	10.09	"	0.37
				10.10	9.72	0.38

Molecular osmotic pressure, 25.20.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.040.

Table VIII.

0.4 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $47^{\circ}.95$; (2) at conclusion of expr., $47^{\circ}.95$; loss, 0. *Manometer*: No. 13; volume of nitrogen, 432.33; displacement, 0. Cell used, D₃. Resistance of membrane, 366,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.30. Time of setting up cell, 4.00 P. M., Oct. 26, 1908.

Time. Oct. 27.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
12.00 M.	25°.00	25°.00	40.96	10.16	9.72	0.44
9.00 P.M.	25°.00	25°.05	41.13	10.12	"	0.40
Oct. 28.						
9.00 A.M.	25°.00	24°.95	41.14	10.12	"	0.40
5.00 P.M.	25°.00	24°.95	41.11	10.13	"	0.41
				10.13	9.72	0.41

Molecular osmotic pressure, 25.33.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.042.

Table IX.

0.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 58°.60; (2) at conclusion of expr., 58°.60; loss, 0. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0.05 mm. Cell used, B₃. Resistance of membrane, 140,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.4. Time of setting up cell, 5.00 P.M., May 25, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 26.						
9.00 A.M.	25°.00	25°.00	35.95	12.77	12.15	0.62
11.40 P.M.	25°.00	25°.10	36.01	12.76	"	0.61
May 27.						
9.00 A.M.	25°.00	25°.10	36.09	12.73	"	0.58
1.00 P.M.	25°.00	25°.20	36.09	12.73	"	0.58
				12.75	12.15	0.60

Molecular osmotic pressure, 25.50.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.049.

Table X.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.60; (2) at conclusion of expr., 58°.60; loss, 0. *Manometer:* No. 9; volume of nitrogen, 433.07; displacement, 0.07 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.70. Time of setting up cell, 5.00 P. M., May 25, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 26.						
9.00 A.M.	25°.00	25°.00	33.05	12.70	12.15	0.55
8.00 P.M.	25°.00	25°.60	33.03	12.72	"	0.57
May 27.						
9.00 A.M.	25°.00	25°.10	33.08	12.70	"	0.55
1.00 P.M.	25°.00	25°.20	33.05	12.71	"	0.56
				12.71	12.15	0.56

Molecular osmotic pressure, 25.42.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.046.

Table XI.

0.6 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $69^{\circ}.0$; (2) at conclusion of expr., $69^{\circ}.0$; loss, 0. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, Λ_3 . Resistance of membrane, 50,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.19. Time of setting up cell, 5.00 P. M., May 25, 1908.

Time.	Temperature.		Volume N_2	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 26.						
9.00 A.M.	$25^{\circ}.00$	$25^{\circ}.00$	25.65	15.43	14.58	0.85
8.00 P.M.	$25^{\circ}.00$	$25^{\circ}.60$	25.64	15.45	"	0.87
May 27.						
9.00 A.M.	$25^{\circ}.00$	$25^{\circ}.10$	25.67	15.43	"	0.85
1.00 P.M.	$25^{\circ}.00$	$25^{\circ}.20$	25.70	15.41	"	0.83
				15.43	14.58	0.85

Molecular osmotic pressure, 25.72.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.058.

Table XII.

0.6 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $69^{\circ}.1$; (2) at conclusion of expr., $69^{\circ}.1$; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, C_3 . Resistance of membrane, 87,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 13.91. Time of setting up cell, 4.30 P. M., June 8, 1908.

Time.	Temperature.		Volume N_2	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 8.						
11.00 P.M.	$25^{\circ}.00$	$25^{\circ}.20$	29.91	15.42	14.58	0.84
June 9.						
9.00 A.M.	$25^{\circ}.00$	$25^{\circ}.10$	29.93	15.41	"	0.83
11.00 P.M.	$25^{\circ}.00$	$25^{\circ}.30$	29.99	15.39	"	0.81
June 10.						
1.00 P.M.	$25^{\circ}.00$	$25^{\circ}.20$	29.95	15.41	"	0.83
				15.41	14.58	0.83

Molecular osmotic pressure, 25.68.

Molecular gas pressure, 24.30.

Ratio of osmotic to gas pressure, 1.057.

Table XIII.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.2; (2) at conclusion of expr., 79°.1; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 5; volume of nitrogen, 471.94; displacement, 0. Cell used, B₃. Resistance of membrane, 161,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.61. Time of setting up cell, 5.00 P. M., June 15, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 15.						
10.30 P.M.	25°.00	25°.10	25.70	18.01	17.02	0.99
June 16.						
10.00 A.M.	25°.00	24°.90	25.66	18.04	"	1.02
5.00 P.M.	25°.00	25°.00	25.67	18.03	"	1.01
June 17.						
10.00 A.M.	25°.00	24°.80	25.73	17.99	"	0.97
				18.02	17.02	1.00

Molecular osmotic pressure, 25.74.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.059.

Table XIV.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.2; (2) at conclusion of expr., 79°.1; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0. Cell used, A₃. Resistance of membrane, 60,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.84. Time of setting up cell, 5.00 P. M., June 15, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 15.						
10.30 P.M.	25°.00	25°.10	22.08	17.98	17.02	0.96
June 16.						
10.00 A.M.	25°.00	24°.90	22.03	18.03	"	1.01
5.00 P.M.	25°.00	25°.00	22.04	18.02	"	1.00
June 17.						
10.00 A.M.	25°.00	24°.80	22.06	17.99	"	0.97
				18.01	17.02	0.99

Molecular osmotic pressure, 25.73.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.058.

Table XV.

0.8 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $88^{\circ}.8$; (2) at conclusion of expr., $88^{\circ}.8$; loss, 0. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.03 mm. Cell used, B₃. Resistance of membrane, 139,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.9. Time of setting up cell, 5.00 P. M., June 6, 1908.

Time.	Temperature.		Volume N ₂	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 7.						
1.00 P.M.	25° .00	24° .70	22.38	20.75	19.45	1.30
11.00 P.M.	25° .00	24° .80	22.38	20.74	"	1.29
June 8.						
10.00 A.M.	25° .00	24° .80	22.38	20.74	"	1.29
3.30 P.M.	25° .00	24° .90	22.38	20.75	"	1.30
				20.75	19.45	1.30

Molecular osmotic pressure, 25.94.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $88^{\circ}.8$; (2) at conclusion of expr., $88^{\circ}.6$; loss, $0^{\circ}.2 = 0.23$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.33; displacement, 0.7 mm. Cell used, D. Resistance of membrane, 183,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.91. Time of setting up cell, 5.00 P. M., June 6, 1908.

Time.	Temperature.		Volume N ₂	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 8.						
10.00 A.M.	25° .00	24° .80	20.54	20.71	19.45	1.26
3.30 P.M.	25° .00	24° .90	20.54	20.71	"	1.26
11.00 P.M.	25° .00	25° .20	20.54	20.71	"	1.26
June 9.						
9.00 A.M.	25° .00	25° .10	20.54	20.71	"	1.26
				20.71	19.45	1.26

Molecular osmotic pressure, 25.89.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.065.

Table XVII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $98^{\circ}.5$; (2) at conclusion of expr., $98^{\circ}.35$; loss, $0^{\circ}.15 = 0.15$ per cent. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.02 mm. Cell used, B₃. Resistance of membrane, 138,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.74. Time of setting up cell, 5.00 P. M., June 3, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 4.						
9.00 A.M.	25°.00	24°.9	19.62	23.70	21.88	1.82
9.00 P.M.	25°.00	24°.9	19.64	23.69	"	1.81
June 5.						
9.00 A.M.	25°.00	24°.9	19.64	23.68	"	1.80
3.00 P.M.	25°.00	24°.9	19.64	23.68	"	1.80
				23.69	21.88	1.81

Molecular osmotic pressure, 26.32.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.083.

Table XVIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $98^{\circ}.4$; (2) at conclusion of expr., $98^{\circ}.15$; loss, $0^{\circ}.25 = 0.25$ per cent. *Manometer*: No. 9; volume of nitrogen, 433.07; displacement, 0.06 mm. Cell used, A₃. Resistance of membrane, 51,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, 0.04; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 22.49. Time of setting up cell, 4.00 P. M., June 25, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 26.						
10.00 A.M.	25°.00	25°.20	18.05	23.61	21.88	1.73
5.00 P.M.	25°.00	25°.20	18.04	23.62	"	1.74
June 27.						
10.00 A.M.	25°.00	25°.00	18.04	23.62	"	1.74
1.00 P.M.	25°.00	25°.10	18.02	23.66	"	1.78
				23.63	21.88	1.75

Molecular osmotic pressure, 26.26.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.080.

Table XIX.

1.0 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $107^{\circ}.1$; (2) at conclusion of expr., $107^{\circ}.0$; loss, $0^{\circ}.1 = 0.09$ per cent. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.23 mm. Cell used, B_3 . Resistance of membrane, 283,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.63; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.11. Time of setting up cell, 4.15 P.M., June 18, 1908.

Time.	Temperature.		Volume N_2	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 19.						
9.30 A.M.	$25^{\circ}.00$	$24^{\circ}.90$	15.18	26.33	24.31	2.02
5.00 P.M.	$25^{\circ}.00$	$25^{\circ}.20$	15.20	26.31	"	2.00
10.00 P.M.	$25^{\circ}.00$	$25^{\circ}.10$	15.20	26.32	"	2.01
June 20.						
10.30 A.M.	$25^{\circ}.00$	$25^{\circ}.00$	15.20	26.31	"	2.00
				26.32	24.31	2.01

Molecular osmotic pressure, 26.32.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.083.

Table XX.

1.0 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $107^{\circ}.1$; (2) at conclusion of expr., $106^{\circ}.7$; loss, $0^{\circ}.4 = 0.36$ per cent. *Manometer*: No. 5; volume of nitrogen, 471.94; displacement, 0.08 mm. Cell used, A_3 . Resistance of membrane, 257,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.64; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.67. Time of setting up cell, 4.15 P. M., June 18, 1908.

Time.	Temperature.		Volume N_2	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
June 19.						
9.30 A.M.	$25^{\circ}.00$	$24^{\circ}.90$	17.69	26.32	24.31	2.01
5.00 P.M.	$25^{\circ}.00$	$25^{\circ}.20$	17.68	26.36	"	2.05
10.00 P.M.	$25^{\circ}.00$	$25^{\circ}.10$	17.69	26.34	"	2.03
June 20.						
10.30 P.M.	$25^{\circ}.00$	$25^{\circ}.00$	17.70	26.33	"	2.02
				26.34	24.31	2.03

Molecular osmotic pressure, 26.34.

Molecular gas pressure, 24.31.

Ratio of osmotic to gas pressure, 1.084.

Table XXI.—Summary of Results.

Concen- tration.	Temper- ature. 25° 00	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	"	0° 00	0.00	2.56	2.43	0.13	25.63	24.30	1.055
"	"	0° 00	0.00	2.56	2.43	0.13	25.55	24.30	1.051
0.2	"	0° 00	0.00	5.09	4.86	0.23	25.43	24.30	1.046
"	"	0° 00	0.00	5.10	4.86	0.24	25.49	24.30	1.049
0.3	"	0° 00	0.00	7.58	7.29	0.29	25.27	24.30	1.040
"	"	0° 00	0.00	7.55	7.29	0.26	25.17	24.30	1.036
0.4	"	0° 00	0.00	10.10	9.72	0.38	25.20	24.30	1.040
"	"	0° 00	0.00	10.13	9.72	0.41	25.33	24.30	1.041
0.5	"	0° 00	0.00	12.75	12.15	0.60	25.50	24.30	1.049
"	"	0° 00	0.00	12.71	12.15	0.56	25.42	24.30	1.046
0.6	"	0° 00	0.00	15.43	14.58	0.85	25.72	24.30	1.058
"	"	0° 00	0.00	15.41	14.58	0.83	25.68	24.30	1.057
0.7	"	0° 10	0.01	18.02	17.02	1.00	25.74	24.31	1.059
"	"	0° 10	0.01	18.01	17.02	0.99	25.73	24.31	1.058
0.8	"	0° 00	0.00	20.75	19.45	1.30	25.94	24.31	1.067
"	"	0° 20	0.03	20.71	19.45	1.26	25.89	24.31	1.065
0.9	"	0° 15	0.02	23.69	21.88	1.81	26.32	24.31	1.083
"	"	0° 25	0.04	23.63	21.88	1.75	26.26	24.31	1.080
1.0	"	0° 10	0.01	26.32	24.31	2.01	26.32	24.31	1.083
"	"	0° 40	0.05	26.34	24.31	2.03	26.34	24.31	1.084

Table XXII.—Summary of Results. Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.
0.1	25° 00	0° 00	0.00	2.56	2.43	0.13
0.2	"	0° 00	0.00	5.10	4.86	0.24
0.3	"	0° 00	0.00	7.57	7.29	0.28
0.4	"	0° 00	0.00	10.12	9.72	0.40
0.5	"	0° 00	0.00	12.73	12.15	0.58
0.6	"	0° 00	0.00	15.42	14.58	0.84
0.7	"	0° 10	0.01	18.02	17.02	1.00
0.8	"	0° 10	0.015	20.73	19.45	1.28
0.9	"	0° 20	0.03	23.66	21.88	1.78
1.0	"	0° 20	0.03	26.33	24.31	2.02

142.24 - 133.69

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	25.59	24.30	1.053
0.2	25.46	24.30	1.048
0.3	25.22	24.30	1.038
0.4	25.27	24.30	1.041
0.5	25.46	24.30	1.048
0.6	25.70	24.30	1.058
0.7	25.74	24.31	1.059
0.8	25.92	24.31	1.066
0.9	26.29	24.31	1.082
1.0	26.33	24.31	1.084

Tables XXIII. and XXIV. give a summary of the progress which has been made, up to the present time, in our attempt to ascertain the temperature coefficient of the osmotic pressure of cane sugar solutions. The first of these (XXIII.) gives the pressures which were obtained in the vicinity of 0°, between 4° and 5°, at 10°, 15°, and, more recently, at 25°. As stated in the beginning of this paper, the first two series (I. and II.) have been discarded because they were made while the method was still in a very imperfect condition, while Series III. and IV., at 0° and 4°-5°, are retained only until we are able to repeat them under the present improved conditions. Series V., VI., and VII. were carried through after the method had been developed to a fairly satisfactory state. It will be seen that the *total pressures* (horizontal line No. 1) increase with

Table XXIII.—Osmotic Pressures. Series III.—VII.

	Concen- tration.	Series III. Pressures. 0°.	Series IV. Pressures. 4-5°.	Series V. Pressures. 10°.	Series VI. Pressures. 15°.	Series VII. Pressures. 25°.
1. Total pressures	0.1	2.42	2.40	2.44	2.48	2.56
2. Mean molecular osmotic pressures	0.2	4.79	4.75	4.82	4.91	5.10
3. Mean molecular gas pressures	0.3	7.11	7.07	7.19	7.33	7.57
4. Mean ratio of osmotic to gas pressure	0.4	9.35	9.43	9.58	9.78	10.12
5. Mean loss in rotation (per cent)	0.5	11.75	11.82	12.00	12.29	12.73
	0.6	14.12	14.43	14.54	14.86	15.42
	0.7	16.68	16.79	17.09	17.39	18.02
	0.8	19.15	19.31	19.75	20.09	20.73
	0.9	21.89	22.15	22.28	22.94	23.66
	1.0	24.45	24.53	25.06	25.42	26.33
		131.71	132.68	134.75	137.49	142.24
		23.95	24.12	24.50	24.98	25.70
		22.29	22.65	23.09	23.50	24.30
		1.074	1.065	1.061	1.064	1.064
		1.73	1.45	0.22	0.10	0.20

Table XXIV.—Mean Ratios of Osmotic to Gas Pressures.
Series III.—VII.

Concentration.	Series III. Ratios. 0°.	Series IV. Ratios. 4°-5°.	Series V. Ratios. 10°.	Series VI. Ratios. 15°.	Series VII. Ratios. 25°.	Series V-VII. Mean ratios.
0.1	1.085	1.060	1.056	1.053	1.053	1.054
0.2	1.074	1.045	1.043	1.045	1.048	1.045
0.3	1.064	1.041	1.038	1.040	1.038	1.039
0.4	1.049	1.042	1.037	1.040	1.041	1.039
0.5	1.055	1.043	1.040	1.046	1.048	1.045
0.6	1.056	1.059	1.050	1.055	1.058	1.054
0.7	1.070	1.060	1.058	1.058	1.059	1.058
0.8	1.074	1.067	1.069	1.069	1.066	1.068
0.9	1.091	1.081	1.073	1.085	1.082	1.080
1.0	1.097	1.084	1.085	1.083	1.084	1.084

rising temperature—from 131.71 atmospheres at 0° to 142.24 atmospheres at 25°. There is also, of course, a corresponding increase in the mean molecular osmotic pressures (horizontal line No. 2). The corresponding mean molecular gas pressures are given, for purposes of comparison, in horizontal line No. 3, while the mean ratios of osmotic to gas pressure, calculated from the aggregate pressure of each series (line No. 1) are recorded in line No. 4. The figures in this line (No. 4) will show at a glance how nearly the observed osmotic pressures appear to follow the law of Gay-Lussac for gases. If they obey the law, the ratios in question should be constant within the limits of necessary experimental errors. Except in the case of Series III.—the earliest of those which are included in the table—they are strikingly concordant. At 15° and 25°, they are identical.

In line No. 5 (Table XXIII.), the mean loss in rotation is given. It will be seen that this was relatively large in the earlier series (III. and IV.), and very small in the later ones (V., VI., and VII.). The loss in rotation is a fair measure of the excellence of the method, although, as we have pointed out elsewhere, it probably exceeds at all times the uncertainty of the results.

In Table XXIII., the aggregate of the pressures of each series has been treated as a unit because by so doing¹ "certain

¹ THIS JOURNAL, 40, 211.

discrepancies observable among the individual concentrations are prevented from obscuring the general trend of the values." Table XXIV. is introduced to show how the individual concentrations have been found to behave with respect to the ratio of osmotic to gas pressure. Here again the ratios for each individual concentration should be found to be constant, if osmotic pressure obeys the law of Gay-Lussac. A comparison of the figures in the horizontal lines will show that they differ but little among themselves except in the cases of the earliest series (III. and IV.). A particular discussion of the relations revealed in Table XXIV. will be postponed until we have completed the work at 20° and 30°, and have repeated Series III. and IV. We shall also repeat certain portions of the work at 10°, 15°, and 25°. This will be done wherever a ratio appears to differ markedly from the other ratios of the same concentration. An instance of this kind will be noted in the case of the 0.9 normal solution of Series V., where the ratio of osmotic to gas pressure was found to be 1.073 (see table), while the ratios at 4°-5°, 15°, and 25° are 1.081, 1.085, and 1.082. The method is already quite capable of testing the reality of such apparent discrepancies.

JOHNS HOPKINS UNIVERSITY,
November 1, 1908.

THE PRESENT STATUS OF THE SOLVATE THEORY.

[TWENTY-THIRD COMMUNICATION.]

By HARRY C. JONES.

(This investigation has for the most part been carried out with the aid of Grants awarded by the Carnegie Institution of Washington.)

This work has been in progress continuously for ten years, and the results obtained published in various scientific journals. It now seems desirable to bring together in one compact whole the more important facts established, and the more important conclusions reached.

This entire work is the outcome, directly or indirectly, of an observation, made in 1898 by Jones and Ota,¹ that the molecular

¹ THIS JOURNAL, 22, 5 (1899).

lowering of the freezing point of water produced in concentrated solutions of certain electrolytes increases from a certain concentration, not only with the dilution, *but also with the concentration.*

This fact was directly at variance with the ideas which then prevailed in reference to the nature of solutions, and could be dismissed only with the unsatisfactory statement that the laws which obtain for dilute solutions do not hold for concentrated solutions, a statement which, of course, explained nothing. The fact that the molecular lowering of the freezing point increased with increase in concentration, and acquired a value in fairly concentrated solutions that was often much greater than the theoretical molecular lowering produced by the completely dissociated electrolyte, merited careful study. These results obtained by Jones and Ota were not published in their paper. Similar observations were, however, made a little later by Jones and Knight¹ in their study of aqueous solutions of double salts. They measured the freezing point lowerings produced by the three double chlorides—ammonium magnesium chloride, sodium zinc chloride, and strontium cadmium chloride—and from these results calculated the molecular lowerings. The following data² for two salts will show what was obtained:

NH ₄ Cl.MgCl ₂		2NaCl.ZnCl ₂	
Volume.	Molecular lowering.	Volume.	Molecular lowering.
1.92	9.48	3.03	12.27
3.84	8.71	6.06	11.84
7.68	8.52	12.12	11.71
15.36	8.63	24.24	11.84
30.72	8.89	48.48	12.47
61.44	9.31		
122.88	9.65		

The molecular lowerings are greater in the more concentrated solutions, decrease with increase in dilution to a minimum, and then increase from this point with the dilution. There is a minimum in the curve expressing the relation between

¹ THIS JOURNAL, 22, 128 (1899).

² *Ibid.*, 22, 110 (1899).

concentration and molecular lowering of the freezing point.

Having established the existence of a minimum in the freezing point curve for a number of substances, Jones and Knight left this question here and continued the investigation of another problem upon which they were engaged, and to which the above line of work was at that time subordinate.

Sufficient observations had, however, been made to show that here was a phenomenon meriting careful study, and which would probably lead to something of importance if thoroughly investigated.

Work of Jones and Chambers.

Jones and Chambers¹ then took up this problem in a systematic manner. On examining the literature of freezing point lowerings produced in concentrated solutions, they found that a few observations were recorded which were similar in character to those made in this laboratory. Arrhenius² had shown that a few chlorides, such as those of calcium, strontium, and magnesium, and cadmium iodide, showed a minimum in the molecular lowering of the freezing point with change in concentration, and similar results had been obtained with three or four organic compounds, while Loomis³ had discovered a corresponding minimum for hydrochloric acid and magnesium chloride.

We found that the number of cases where a minimum in the freezing point lowering had been observed was thus very small, and it was not even suspected that this was a general property of substances. Further, the cases observed were so isolated that no relation between this and any other property had been pointed out.

Jones and Chambers⁴ raised these questions: "Are these apparently abnormal results peculiar to a substance here and there, regardless of its chemical nature, or are they confined to some group of compounds? Do substances which are chemically allied show this peculiarity?"

¹ THIS JOURNAL, 28, 89 (1900).

² Z. physik. Chem., 2, 496 (1887).

³ Wied. Ann., 87, 503 (1896).

⁴ THIS JOURNAL, 28, 92 (1900).

Since Jones and Knight had observed the minimum in the freezing point curves for one or two members of the calcium group, Jones and Chambers turned their attention to the chlorides and bromides of calcium, strontium, barium, magnesium, and cadmium. All of these substances, except the salts of cadmium, showed the minimum in the freezing point curves, at concentrations ranging from 0.1 to 0.2 normal.

The conductivities of these solutions were measured to see whether the conductivity curves showed any corresponding minimum. No such minimum was found.

Jones explained these results in the following words:¹ "How is it then possible to account for these abnormally great depressions of the freezing point? There appears to us to be only one way. In concentrated solutions these chlorides and bromides must take up a part of the water, forming complex compounds with it, and thus removing it from the field of action as far as freezing point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit, or as one molecule, in lowering the freezing point of the remaining water. But the total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all of the freezing point results obtained."

It was pointed out at this time² that practically all of those substances in which a freezing point minimum had been observed were strongly hygroscopic, *i. e.*, had the power to combine readily with water out of solution, and that there was probably a connection between this property and the power to combine with water when dissolved in it. It "should

¹ THIS JOURNAL, 23, 103 (1900).

² *Ibid.*, 23, 104 (1900).

be observed, in connection with the explanation we have offered of these abnormal results, that the chlorides and bromides of the alkaline earths are, generally, very hygroscopic substances, resembling sulphuric acid in their power of attracting water. It may be due to this property that they combine with water to such an extent in concentrated solutions."

When the above suggestion was made I had grave doubts whether it was the true explanation of the phenomena that had been observed, since at that time I was not at all a believer in hydration or combination between the solvent and dissolved substance. The above suggestion was made as the only rational explanation of the results that I could think of. "We¹ do not put forward the above suggestion to account for our results as a final statement of a theory, but only as tentative, and subject to modification as new facts are brought to light. It does, however, seem to account qualitatively for the experimental facts which have been brought to light."

Work of Chambers and Frazer.

At the suggestion of Jones, and under his guidance, Chambers and Frazer² continued the work of Jones and Chambers. Impressed by the fact that it is hygroscopic substances which show a pronounced freezing point minimum, Chambers and Frazer studied other hygroscopic compounds, such as hydrochloric and phosphoric acids, sodium acetate, zinc chloride, strontium iodide, cadmium iodide, and copper sulphate.

All of the substances investigated showed a more or less pronounced minimum in the freezing point curve, and it will be recognized that all of them have more or less attraction for water—are, as we say, hygroscopic.

The conclusion reached by Chambers and Frazer was that the theory advanced by Jones and announced in the paper by Jones and Chambers accounted for all of the facts that they had discovered. They further added that this seemed to them to be the only reasonable explanation of these facts.

¹ THIS JOURNAL, 23, 105 (1900).

² *Ibid.*, 23, 512 (1900).

The earlier investigations, then, showed that the minimum in the freezing point curve was not an isolated phenomenon, limited to a few substances, but was manifested by a large number of compounds. The question then arose: Is the phenomenon a general one? Do substances in general give too great lowering of the freezing point in concentrated solutions?

Work of Getman.

To test this point Jones and Getman¹ took up the problem in a broad way, and measured the freezing point lowerings, conductivity, and refractivity of a fairly large number of typical compounds. These included: hydrochloric acid and the chlorides of lithium, ammonium, sodium, potassium, calcium, strontium, and barium; nitric acid and the nitrates of lithium, ammonium, sodium, and potassium; sulphuric acid and the sulphates of ammonium, sodium, and potassium; sodium and potassium carbonates; phosphoric acid and potassium dihydrogen phosphate; and sodium and potassium hydroxides.

The conclusion² drawn from this work was "that with but few exceptions electrolytes in general give abnormal molecular depressions of the freezing point. Among these exceptions are sodium, potassium, and ammonium nitrates, and potassium dihydrogen phosphate.

"Among the chlorides we observe that those of the second group in the Periodic System give greater molecular depressions than those of the first group."

It was pointed out that the conductivity curves for all of the substances included in this investigation are normal, showing nothing corresponding to the minimum in the freezing point curves. The refractivity curves were practically straight lines.

The few boiling point curves obtained showed also a more or less pronounced minimum. It was noted in this investigation that the *minimum in the boiling point curves was at a greater concentration than in the freezing point curves.* And

¹ Z. physik. Chem., 46, 244 (1903). Phys. Rev., 18, 146 (1904).

² Z. physik. Chem., 46, 244 (1903).

it was pointed out that this is just what would be expected if this minimum was due to hydration. At the higher temperature the hydrates would be less stable, and a greater concentration would, therefore, be required to produce enough hydration to show the minimum in the curve. We shall see later that this is a point of some importance in connection with the evidence for the existence of hydrates in aqueous solutions.

Through a Grant generously awarded by the Carnegie Institution, Jones and Getman¹ were enabled to extend their earlier work to a larger number and greater variety of substances. In their second investigation they included the chlorides, nitrates, and sulphates of manganese, nickel, copper, and aluminium.

Boiling point measurements were also made with potassium iodide, sodium iodide, ammonium iodide, cadmium iodide, and sodium bromide, in ethyl alcohol.

Up to this time the freezing point lowerings of forty-nine compounds had been studied, and only nine failed to show a minimum in the freezing point curves. A number of these nine substances, however, gave abnormally great depressions of the freezing point in concentrated solutions, so that nearly all of the substances investigated, with the exception of two or three sulphates which are obviously polymerized in concentrated solutions, since their molecular lowerings are less than the constant for water, show abnormally great lowerings of the freezing point in such solutions. A relation was discovered, at this stage of the work, which has proved to be of considerable importance in dealing with the whole problem of hydration in aqueous solutions. On comparing the molecular lowerings of the freezing point, as shown by the various substances, it was seen that there is a relation between the freezing point lowering produced by the different substances and the amounts of water with which they crystallize.

Those substances that crystallize with the largest number of molecules of water of crystallization give the greatest molecular lowering of the freezing point of water in concentrated solutions.

¹ THIS JOURNAL, 31, 303 (1904).

This relation is of fundamental importance as bearing on the hydrate theory; indeed, is one of the strongest arguments in its favor. Those substances that combine with the largest amounts of water out of solution—water of hydration—would be the substances which in solution would combine with the largest amounts of water—would form the most complex hydrates. These would, of course, be the substances which would give the greatest lowerings of the freezing point of water, since the combined water would be removed from the field of action as far as freezing point lowering is concerned.

The evidence for the existence of hydrates seemed, at this time, to be sufficiently well established to make it highly probable that dissolved substances in general combine with more or less of the water in which they are dissolved. It was then a matter of importance to determine, if possible, even the approximate amount of water with which various substances combine, and Jones and Getman attempted to make such calculations.

The molecular lowering was calculated from the observed lowering in the usual way—by dividing the actual lowering by the concentration in terms of normal. Since, however, in concentrated solutions there are not one thousand grams of water in a liter of solution, this must be taken into account. The specific gravities of the solutions were determined, and from these data and the concentrations the amount of water present in a liter of the solution was easily calculated.

The theoretical molecular lowering for a substance at the dilution in question could also be easily calculated. It was necessary to know only the dilution of the solution, and the dissociation at that dilution, and then to apply Raoult's law. The normal molecular lowering for a completely undissociated, unhydrated compound, or the freezing point constant for water, was taken as $1^{\circ}.86$.

"The¹ calculated molecular lowering can now be compared directly with the corrected, observed molecular lowering. If there were no hydration these two values would be equal. The magnitude of the hydration is obtained as follows: The

¹ Carnegie Publication, No. 60, p. 28 (1907).

calculated molecular lowering is divided by the corrected molecular lowering found. This ratio multiplied by 1000 gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

"The difference between this amount of water and 1000 grams is the quantity that is in combination with the dissolved substance, under the conditions that obtain in the solution in question. For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing point constant is calculated for 1000 grams of the solvent, and by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

"If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with one molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

"In order¹ then to be able to calculate the approximate composition of the hydrates formed by any given substance, it is necessary to know the following quantities:

"The lowering of the freezing point produced by the dissolved substance.

"The conductivity of the solution as an approximate measure of its dissociation.

"The specific gravities of the solutions, in order to calculate the difference between 1,000 grams of water and the amount contained in a liter of the solution."

Even with all of this data it is, of course, possible to calculate only the approximate composition of the hydrates formed,

¹ Carnegie Monograph, No. 60, 28 (1907).

since there are some assumptions made that are only approximations. This is especially true, as has been repeatedly pointed out, for the law of Raoult, which, in all probability, holds only approximately for concentrated solutions. However, the results obtained for the various substances are, in all probability, of the right order of magnitude, and show, at least, the correct relative hydrating power of the various compounds.

At this time Jones and Getman calculated, on the above basis, the approximate composition of the hydrates formed by salts of copper and aluminium. The complexity of the hydrates formed by these salts was found to be great—as much as forty or fifty molecules of water combining with one molecule of the salt. The most interesting fact brought out by these calculations was that the complexity of the hydrate increases with the dilution of the solution, and with fair regularity from the most concentrated to the most dilute solution investigated. This is, of course, just what would be expected from the law of mass action applied to the formation of these hydrates—the larger the amount of water present per molecule of the dissolved substance, the greater the amount of water combined with a dissolved molecule or the resulting ions.

Having found that water combines with a large number of dissolved substances, the question arose: Is this property limited to water? Do we have only hydration, or do other solvents also have the power of combining with substances dissolved in them?

Jones and Getman¹ extended their work from aqueous to nonaqueous solutions. They worked with solutions of lithium chloride, lithium nitrate, and calcium nitrate in ethyl alcohol, using the boiling point method, and plotted their results against concentrations as abscissae and molecular rise in the boiling points as ordinates.

Their work furnished evidence that the alcohol combines with the dissolved salt—that alcoholates are formed. The evidence furnished was, however, purely qualitative, the

¹ THIS JOURNAL, 32, 338 (1904).

results obtained not enabling them to calculate even the approximate composition of the alcoholates.

Having studied a few salts in a solvent other than water, and a large number of salts in water, Jones and Getman¹ took up the problem of nonelectrolytes and organic acids, to see whether these substances combine with any appreciable amount of water when dissolved in that solvent.

The results obtained are perfectly clean cut. Of thirteen nonelectrolytes, only one, glycerol, had any very marked power to combine with water. Glycerol has large hydrating power. A few other nonelectrolytes, such as cane sugar and fructose, also have some considerable power to combine with water, but this is not of the same order of magnitude as that shown by glycerol.

"The question as to whether the alcohols have any very marked hydrating power is of interest in the light of the composition which has been assigned to these hydrates by certain investigators."

It was found that while methyl and ethyl alcohols have slight power to combine with water, this is very small in comparison with the hydrating power of many salts.

It having been shown that certain of the strong mineral acids have considerable power to combine with water, the question arose: Is this power possessed by the organic acids? A number of them were studied from the standpoint of hydration, and it was found that none of them had any appreciable power to combine with water. In comparison with the mineral acids, the hydrating power of the organic acids is negligible. If the hydrating power of mineral acids is due to the hydrogen ions, which is questionable, then the organic acids have but little hydrating power because there are only a few hydrogen ions present—because they are only little dissociated.

A fairly broad discussion of the subject of hydration in general, as worked out by Jones and Getman, was prepared just before Dr. Getman left this laboratory.² The work was sufficiently extended by this time to make it possible to see

¹ Carnegie Monograph, No. 60, 101 (1907).

² *Z. physik. Chem.*, **49**, 385 (1904).

the real significance and importance of the relation between freezing point lowering and water of crystallization. Nearly seventy compounds had been studied—salts of potassium, sodium, lithium, ammonium, calcium, strontium, barium, magnesium, zinc, cadmium, manganese, nickel, cobalt, copper, aluminium, chromium, and iron.

A number of these salts, notably those of potassium and ammonium, crystallize without water. Some of the sodium salts are anhydrous, while others crystallize with water. The salts of barium crystallize with two molecules of water; those of calcium, strontium, magnesium, nickel, and cobalt, with six molecules of water each, while the nitrates of aluminium, chromium, and iron crystallize with from eight to nine molecules of water.

Here then was an excellent opportunity to test the relation between freezing point lowering and water of crystallization. The curves expressing the relation between concentration and freezing point lowering were plotted; the chlorides on one sheet, the bromides on a second sheet, the iodides on a third, and the nitrates on a fourth.¹

On the chloride sheet, all of those chlorides were introduced whose curves could be inserted without undue crowding. At the bottom of the sheet fell those chlorides that crystallize without water—potassium, sodium, and ammonium—and the three curves corresponding to these compounds were almost coincident. The chloride of lithium, a binary electrolyte with two molecules of water of crystallization, came next above, and then the chloride of barium, a ternary electrolyte with two molecules of crystal water.

Above the curve corresponding to barium chloride, and some distance above it, fell the curves for strontium, calcium, and magnesium chlorides, each crystallizing with six molecules of water. These three chlorides, again, ran close together.

Much farther above on the same sheet we find the chlorides of aluminium and iron—quaternary electrolytes, each crystallizing with six molecules of water.

The relation, then, between water of crystallization and

¹ Carnegie Publication, No. 60, p. 21 (1907).

lowering of freezing point was nearly perfect, as far as the chlorides were concerned.

The bromides, as already stated, were plotted on a corresponding sheet. The anhydrous bromides of cadmium and potassium fell near the bottom of the sheet. Sodium bromide with two molecules of water was somewhat above the bromide of potassium. *The curve for lithium bromide was considerably above that of sodium.

Barium bromide—a ternary electrolyte with two molecules of water—occupies a considerably higher position on the sheet than lithium bromide, while for the bromides of strontium, calcium, and magnesium, each with six molecules of water of crystallization, the curves are close together and well above that of the bromide of barium.

The relations for the bromides are, then, as satisfactory as for the chlorides.

Exactly similar relations are shown on the iodide sheet. The curves for the anhydrous iodides of cadmium and potassium are at the bottom; that for sodium iodide, with two molecules of water, next above; and still higher is the curve for lithium iodide with three molecules of crystal water. The curve for the ternary iodide of barium, with its two molecules of water of crystallization, lies considerably above that for lithium iodide, while at the top of the sheet we have the curves for the iodides of strontium and calcium, each crystallizing with six molecules of water.

The curve sheet for the nitrates is even more convincing, if possible, than those already considered because of certain facts in connection with the nitrate of calcium, which will be considered below.

The curves for the anhydrous nitrates of sodium, potassium, and ammonium fall together at the bottom of the sheet. Then comes lithium nitrate with two molecules of water, and then the nitrate of calcium, which crystallizes with four molecules of water. The ternary nitrate of calcium, with four molecules of water, lies almost exactly half way between lithium nitrate with two molecules and a number of nitrates,

each with six molecules of crystal water. This relation is, certainly, most satisfactory.

The nitrates of manganese, cobalt, nickel, zinc, and magnesium all crystallize with six molecules of water, and their curves all occupy very nearly the same position on the nitrate curve sheet. The curve for the nitrate of copper is a little higher than would be expected.

The nitrates of aluminium, iron, and chromium crystallize, the first with eight, and the last two with nine molecules of water each. Their curves are very near the top of the sheet, lying far above those of any other nitrate studied. It should be noted that these salts not only crystallize with a larger amount of water than any other nitrates brought within the scope of this investigation, but are also quaternary electrolytes.

So much for the relations between the *different salts of the same acid with different metals*. Certain relations of equal interest and importance were found to exist *between the salts of the same metal with different acids*.

"If" we compare the results for the chlorides, bromides, iodides, and nitrates, we shall find abundant evidence bearing on the relation between freezing point lowering and water of crystallization. Chlorides, bromides, iodides, and nitrates that crystallize without water all show a molecular lowering of between 3 and 4, and this increases very slightly, if at all, with the concentration. As far as the comparison can be carried, lithium chloride, with 2 molecules of water, gives less lowering than lithium bromide or lithium iodide with 3 molecules of water, and just about the same lowering as lithium nitrate with 2 molecules of water of crystallization.

"Lithium bromide, with 3 molecules of water, gives about the same lowering as lithium iodide, which has the same amount of water of crystallization. Sodium bromide, with 2 molecules of water, gives very nearly the same lowering as sodium iodide, which has the same number of molecules of water of crystallization.

"Barium chloride has the same number of molecules of water

¹ Carnegie Monograph, No. 60, p. 25 (1907).

of crystallization as the bromide and iodide. Since barium chloride has only a slight solubility in water, comparison of freezing point lowerings must be limited to dilute solutions. The freezing point lowerings of the three salts are just about the same in the dilute solutions, although in the more concentrated solutions the iodide shows greater lowering than the bromide.

"If we compare the chlorides, bromides, and iodides of the alkaline earths, which contain each 6 molecules of water of crystallization, we shall find that the lowerings of the freezing point produced by them are all of the same order of magnitude. We shall, however, see that the bromides give somewhat greater lowering than the chlorides, and the iodides even greater lowering than the bromides.

"As far as comparisons can be made it seems that the nitrates produce about the same lowerings as the corresponding chlorides with an equal number of molecules of water of crystallization, and, therefore, somewhat less than the corresponding bromides and iodides.

"The quaternary chlorides of aluminium and iron can not be compared, at present, with respect to their freezing point lowering, with the corresponding bromides and iodides, because the latter have not yet been investigated.

"A comparison of the lowerings produced by the chlorides of iron and aluminium, containing 6 molecules of crystal water, with the nitrates of the same metals which have a larger amount of water of crystallization will show a somewhat greater lowering, at the same concentrations, for the nitrates.

"Thus, the relation between the lowering of the freezing point of water produced by salts and their water of crystallization comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids."

Since, as will be seen later, Jones and Bassett call attention to the large number of examples illustrating the fact that water of crystallization is a function of the temperature at which the salt crystallizes, it might be concluded that the

above relations are not strictly true, but depend upon the temperatures at which the salts crystallize. That this is not the case will be seen if we consider that the amounts of water of crystallization attributed to the compounds are the amounts with which the several salts crystallize under ordinary conditions, *i. e.*, under as nearly comparable conditions as possible, and which are, therefore, directly comparable with one another.

Work of Bassett.

Jones and Bassett¹ plot the results referred to above in the form of curve sheets—the chlorides upon one sheet, the bromides upon another, the iodides upon a third, and the nitrates upon a fourth. An examination of these curve plates will bring out at a glance the relation between water of crystallization and lowering of the freezing point. Concentrations are plotted as the abscissae and molecular lowerings of the freezing point as the ordinates. The relative positions of the curves upon any one sheet, corresponding to the several salts of a given acid, are conditioned by the number of molecules of water with which the various salts crystallize.

The relations are so satisfactory and general that it would be a simple matter to determine quite closely the number of molecules of water with which an unknown chloride, for example, crystallizes, by determining its molecular lowering of the freezing point of water.

This line of evidence bearing upon the hydrate theory, as advanced by Jones, is so satisfactory and general, that it is regarded as a strong argument in favor of the general correctness of this theory.

The work of Jones and Bassett had to do primarily with the determination of the approximate composition of the hydrates formed by a large number of substances. They were able to calculate, more accurately than had hitherto been done, the composition of the hydrates, and found that the complexity of the hydrates increased with the dilution of the solution, as would be expected from the law of mass action.

¹ THIS JOURNAL, **33**, 536-539 (1905). Jones: J. Chim. Phys., **3**, 478-481 (1905).

In general a fairly regular increase was observed; indeed, as regular as could be expected, considering the large number of experimentally determined values involved in each of these calculations, and, therefore, the large number of experimental errors which were necessarily introduced. These errors would be of a very considerable order of magnitude, especially in the more dilute solutions.

Jones and Bassett, in their earlier work, pointed out another line of evidence bearing upon the hydrate theory. If hydrates exist in solution they become more and more unstable with rise in temperature. This is characteristic of exothermic reactions in general, and is shown to apply to hydrates by the fact that at the boiling points of saturated solutions practically all of the water is removed, except that with which the compound crystallizes at the temperature in question.

The converse of the above can readily be tested by experimental facts. *These hydrates become more and more stable the lower the temperature*; consequently, dissolved substances would crystallize with more and more water the lower the temperature at which the crystals form.

That such is, in general, true is well known to every one; but how general such a relation is may not be fully appreciated by those who have not looked closely into the facts.

Jones and Bassett¹ examined the literature to see how many cases had been studied in this connection, and were surprised at the large number of striking examples upon record. A few examples will make this clear:

Salt with water of crystallization.	Temperature of crystallization.
$\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$	-10° to -12°
$\text{MgCl}_2 \cdot 10\text{H}_2\text{O}$	$+20^\circ$
$\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$	Above $+20^\circ$
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Higher temperatures
$\text{MnCl}_2 \cdot 12\text{H}_2\text{O}$	-48°
$\text{MnCl}_2 \cdot 11\text{H}_2\text{O}$	-21° to -37°
$\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$	-21°
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	$+15^\circ$
$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$	$+20^\circ$

¹ Z. physik. Chem., **52**, 1231 (1905).

Salt with water of crystallization.	Temperature of crystallization.
$\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	-27°
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-16°
$\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$+58^\circ$ and higher
$\text{CO}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	-29° to -22°
$\text{CO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-22° to $+56^\circ$
$\text{CO}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	$+56^\circ$ to $+91^\circ$
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	-16° to $+20^\circ$
$\text{FeCl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	$+20^\circ$
$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	$+40^\circ$ to $+60^\circ$
$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$	$+60^\circ$ to $+80^\circ$
FeCl_3 , anhydrous	$+80^\circ$ and above

These examples suffice to illustrate the point and to show how regularly water of crystallization decreases with rise in temperature, just as would be expected from the hydrate theory. So far as is known to us, there is not a single exception to this relation on record.

Jones and Bassett carried out experiments which made it highly probable that some very well-known compounds can be made to crystallize with larger amounts of water than had been hitherto supposed possible, by crystallizing them at very low temperatures. These results have not yet been recorded, and will not be until further experimental work on these substances is completed.

Jones and Bassett raise the question as to whether it is the ions or the molecules that form hydrates. Since it had been shown by Jones and Getman that certain nonelectrolytes, such as glycerol, acetamide, fructose, etc., can combine with water, and since such substances in solution are undissociated, it follows that molecules have the power to combine with water.

Since, however, the magnitude of the hydration increases with the dilution of the solution, acquiring a very large order of magnitude in solutions so dilute that they contain mainly ions and only a few molecules, it follows not only that ions have great hydrating power, but in all probability, much greater hydrating power than the molecules. That mole-

cules have hydrating power is further shown by the fact that salts crystallize with water, which is essentially water of hydration. Substances under these conditions are chiefly in the molecular condition, unless we assume that the molecules are sufficiently dissociated in their own water of crystallization to yield enough ions to combine with all of the water brought out of solution as water of crystallization, which is highly improbable.

We must, then, conclude that both molecules and ions can form hydrates, but that the ions have much greater power to combine with water than the molecules when dissolved in that substance.

The nature of the hydrates formed by both electrolytes and nonelectrolytes was discussed by Jones and Bassett. In the hydrates formed by a substance like calcium chloride, for example, the number of molecules of water per molecule of the salt varies all the way from a few to a large number—at least as many as thirty.

This raises the question as to whether we have *all intermediate stages* represented, *i. e.*, a series of hydrates ranging in composition from a very few to at least thirty molecules, as appears from the results to be the case; or whether we have *a few definite hydrates*, and then mixtures of these in varying proportions.

It is impossible at present to decide finally between these two alternatives, since there is apparently no experimental method available for doing so directly. Under these conditions we accept the simpler alternative and regard the hydrates as having all compositions intermediate between the simplest and the most complex. Further, this view, it seems to me, is more in accord with the general properties of solutions, and the *regular changes* which are manifested in such properties as we change the dilution of the solutions.

The stability of the hydrates is not sufficiently great to justify us in calling them definite chemical compounds. It is well known that the more complex hydrates readily break down with rise in temperature, and marked decomposition results from slight changes in temperature, even when such

changes take place at comparatively low temperatures. We would, therefore, scarcely be justified in calling such unstable systems as the hydrates definite chemical compounds.

The later work of Jones and Bassett¹ had to do primarily with the determination of the composition of the hydrates formed by a fairly large number of salts, acids, and bases.

Among the salts are such compounds as chromium chloride, potassium ferrocyanide, potassium ferricyanide, sodium chromate, sodium dichromate, disodium phosphate, ammonium sodium acid phosphate, ammonium cupric chloride, potassium cupric chloride, etc.

Some results were obtained bearing on the way in which potassium ferro- and potassium ferricyanide dissociate.

A number of acids, such as hydrochloric, hydrobromic, nitric, phosphoric, and chromic, were included in this investigation, and also the bases, sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

At the completion of the work of Jones and Bassett, about *one hundred compounds* had been brought within the scope of this investigation as a whole, and about *fifteen hundred solutions* had been worked with. All of the results thus far obtained were found to be in accord with the hydrate theory as proposed by Jones.

Work of West.

An unexpected line of evidence bearing upon the hydrate theory was brought to light by the work of Jones and West² on the temperature coefficients of conductivity, as was pointed out by Jones.³ The conductivity of electrolytes increases rapidly with rise in temperature, as is well known. This is not due to any increase in dissociation with rise in temperature; on the contrary, the dissociation of electrolytes decreases as the temperature is raised. The large positive temperature coefficients of conductivity of electrolytes is then due to the increased velocity with which the ions move at the more elevated temperatures. There are a number of

¹ THIS JOURNAL, 34, 291 (1905).

² *Ibid.*, 34, 357 (1905).

³ *Ibid.*, 35, 445 (1906).

factors coming into play which condition the velocities with which the ions move under a constant driving force. The chief factors would be the size and mass of the ions, and the viscosity of the medium in which they move. At the more elevated temperature the viscosity of the medium would become less and less, and this alone would tend to cause the ions to move the faster, the higher the temperature.

Another factor of great importance as conditioning the temperature coefficients of conductivity is the *decreasing complexity of the hydrate around the ion with rise in temperature*. Since the ion must drag this solvate with it through the solvent, the effect of decreasing the complexity of the solvate would be to decrease the mass of the ion, and, therefore, to increase its velocity.

This conclusion, which is a necessary consequence of the hydrate theory and the instability of hydrates with rise in temperature, can be tested directly by the experimental results obtained by Jones and West.

If the diminishing complexity of the hydrate formed by the ion with rise in temperature plays any important part in conditioning the large temperature coefficient of conductivity, then those ions that form the most complex hydrates would be the ones whose masses would change to the greatest extent with rise in temperature, since the more complex the hydrate the greater the change in its complexity for a given rise in temperature. In a word, *those ions that have the greatest hydrating power would have the largest temperature coefficients of conductivity*.

If we examine the results obtained by Jones and West, we shall see that the above conclusion is strikingly substantiated by the facts.¹ It will be recalled that hydrating power is nearly a linear function of the water of crystallization. Those compounds with the largest amounts of water of crystallization have much larger temperature coefficients of conductivity than those that crystallize with but little or no water.

¹ THIS JOURNAL, 35, 448 (1906).

A corollary to the above conclusion would be that those substances which have approximately the same hydrating power, i. e., which crystallize with the same number of molecules of water, would have approximately the same temperature coefficients of conductivity. This conclusion is also abundantly verified by the facts. If we examine the temperature coefficients obtained by Jones and West, we see that those substances which crystallize with the same amounts of water have temperature coefficients of conductivity of at least the same order of magnitude, and in many cases are very nearly equal.

Since there are other factors than hydration coming into play as conditioning these temperature coefficients, such as the mass and volume of the unhydrated ion, the above agreements between fact and theory are as close as common sense would lead us to expect.

A second conclusion from the hydrate theory, as bearing upon temperature coefficients of conductivity, can also be tested by the results obtained by Jones and West.

The more dilute the solution the more complex the hydrates existing in solution. The more complex the hydrates the greater the change in the complexity with rise in temperature, as we have seen. If the temperature coefficients of conductivity are conditioned to any appreciable extent by the complexity of the hydrates, then the more dilute solutions of a given substance should have larger temperature coefficients of conductivity than the more concentrated.

That such is the case is seen at once by examining the temperature coefficients for any substance at different dilutions. The temperature coefficients become larger and larger the more dilute the solutions, until at a dilution of a thousand liters they are often nearly twice as large as the coefficients for the same substance at two liters, for example.

The conclusions from the hydrate theory are thus substantiated most satisfactorily by the experimental results, and this is, therefore, another line of evidence in favor of the general correctness of the theory.

Work of McMaster.

The work of Jones and McMaster,¹ as bearing on the theory of solvation in solution, is an extension of the work of Jones and Getman, and deals with solutions of certain salts in methyl and ethyl alcohols. The salts in question are lithium chloride, lithium bromide, and lithium nitrate in methyl and in ethyl alcohols, and calcium nitrate in ethyl alcohol. The boiling point method was employed.

The molecular rise in the boiling point was found to increase with the dilution and also with the concentration, passing, therefore, through a minimum, just as the molecular freezing point lowering of water passes through a minimum. The molecular rise not only increased with the concentration, but in the most concentrated solutions had a value almost twice that of the boiling point constant for methyl alcohol, and much larger than the boiling point constant for ethyl alcohol.

These boiling point results in the alcohols could be explained only in terms of the same theory as was applied to the freezing point results in aqueous solutions. Just as in the latter we had hydrates formed, removing a part of the water from the rôle of solvent, so here we have alcoholates, or a part of the alcohol no longer plays the rôle of solvent, but is combined with the dissolved substance.

Attention should be called here to the following facts, which, if not clearly recognized, would lead to confusion. While the complexity of the solvate in combination with any dissolved particle increases with the dilution, as would be demanded by the law of mass action, the *total amount of the solvent combined* with the dissolved substance increases with the concentration of the solution—the more concentrated the solution the smaller the amount of solvent present acting as such.

This accounts for the increase in the molecular lowering of the freezing point, and in the molecular rise in the boiling point, which have been so generally observed.

¹ THIS JOURNAL, 35, 316 (1906).

Dissolved substances, then, combine with the alcohols as they combine with water, though probably not to the same extent.

At this stage in the development of the hydrate theory Jones¹ prepared a brief statement of the evidence that had been obtained up to that time for the correctness of the theory.

Investigations in Mixed Solvents.

The investigations of Jones and his coworkers, Lindsay, Carroll, Bassett, Bingham, Rouiller, McMaster, Veazey, Mahin, and Schmidt,² on the conditions of dissolved substances in mixed solvents, have led to results which bear upon the theory of solvation. This work included the solvents water, methyl alcohol, ethyl alcohol, and acetone, and mixtures of each solvent with all of the others. A large number of salts have been studied in the separate solvents and also in the mixed solvents.

The conductivity of a salt like potassium iodide, in mixtures of water and methyl alcohol, for example, passed through a well-defined *minimum* in a particular mixture of the two solvents. The appearance of this minimum was satisfactorily explained by the facts brought to light by Jones and Murray,³ in their work on the effect of one associated solvent on the association of another associated solvent with which it was mixed. It was shown by them that when two associated solvents, such as water and acetic or formic acid, are mixed, each diminishes the association of the other.

The same conclusion would apply to two such associated solvents as water and methyl alcohol. Since of two such solvents each diminishes the association of the other, each would diminish the dissociating power of the other, and, consequently, a mixture of two such solvents in the proper proportions could easily have less dissociating power than either solvent separately.

A salt dissolved in mixtures of two associated solvents would show a minimum conductivity in that particular mixture

¹ Z. physik. Chem., **55**, 385 (1906).

² Carnegie Publication, No. 80 (1907).

³ THIS JOURNAL, **30**, 193 (1903).

where each solvent diminished the association of the other to a maximum extent, or where, at least, the sum of the effects was a maximum.

When, however, acetone was used as one of the solvents, this minimum did not appear, but, on the contrary, a pronounced *maximum* manifested itself in the conductivity curve, especially when the salt was lithium nitrate or calcium nitrate, and the solvent a mixture of acetone with methyl or ethyl alcohol.

It was shown¹ that this maximum may be due, theoretically, to either of two causes: either to an increase in the dissociation, increasing the number of ions present, or to a diminution in the size of the ionic spheres, which would cause the ions to move more rapidly. One of these possible factors could easily be eliminated. The direct measurement of the dissociation in mixtures of the above-named solvents showed that such mixtures do not dissociate to a greater extent than would be calculated from the dissociating power of the individual solvents. Having eliminated this factor, we must conclude that the conductivity maximum referred to above is produced by a change in the degree of solvation of the ions.

"In² dealing with conductivity in single solvents and in mixtures of these with one another, we must take into account the sizes of the spheres of the solvents around the ions, and any changes in the sizes of these spheres in different mixtures of the solvents.

"Any change in the size of these spheres would produce a change in the effective mass of the ion, and, consequently, a change in the velocity with which it would move.

"The size of the ionic spheres is an important factor in determining conductivity, and changes in the sizes of these spheres in different mixtures of the solvents are the prime factor in conditioning the maximum in the conductivity curve."

The bearing of solvation upon the temperature coefficients of conductivity in nonaqueous and mixed solvents is as im-

¹ Carnegie Publication, No. 80 (1907).

² *Ibid.*, No. 80, p. 222 (1907).

portant as the bearing of hydration upon the temperature coefficients of conductivity in aqueous solutions. In the case of nonaqueous solvents, however, a new phenomenon manifested itself, *i. e.*, *negative temperature coefficients*.

A satisfactory explanation for this was, however, furnished.

Work of Pearce.

Jones and Pearce¹ studied a problem which was suggested by the hydrate theory. They measured the dissociation of electrolytes by both the conductivity and the freezing point methods and compared the results obtained by the two methods.

In terms of the hydrate theory, the dissociation as measured by the freezing point method should be *greater* than as measured by conductivity, and for the following reasons: If a part of the water present is not acting as solvent, but is in combination with the ions of the electrolyte, this would affect the freezing point lowering nearly proportionally, since, over small ranges in concentration freezing point lowering is nearly a linear function of the concentration.

Hydration of the ions would also affect conductivity. The greater the hydration, the greater the mass of the ion, and, consequently, for a constant driving force, the more slowly the ion would move. While the conductivity method would, therefore, not give the true dissociation of the electrolyte, it would be affected by the hydration not linearly, but to a much smaller extent. The dissociation as measured by the freezing point lowering should, therefore, be greater than as measured by the conductivity method.

The work of Pearce included calcium chloride, strontium chloride, magnesium chloride, barium chloride, calcium nitrate, strontium nitrate, magnesium nitrate, barium nitrate, cobalt chloride, cobalt nitrate, copper chloride, copper nitrate, nickel nitrate, aluminium chloride, sodium bromide, hydrochloric, nitric, and sulphuric acids.

Thus, fifteen salts and three strong acids have been brought within the scope of this investigation and the results obtained are strictly in accord with what would have been predicted

¹ THIS JOURNAL, **38**, 683 (1907).

from the hydrate theory. "Since the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex is greater, the more dilute the solution; and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be less than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

"If we compare the values for the dissociation α , obtained, on the one hand by the conductivity method and on the other by the freezing point method, we shall see that in the case of every salt studied, without exception, the dissociation as calculated from the freezing point lowering is higher than the dissociation as calculated from the conductivity measurements."

Another point of interest, and perhaps of some importance, came out as the result of the work of Pearce.

It having been shown that the ions have such large hydrating power, the question arises as to whether the cation or the anion has the greater hydrating power. A careful study of all of the results obtained, comparing the salts with a common cation, and those with a common anion, makes it very probable that hydrating power is primarily a function of the cation.

A relation between *atomic volumes and hydrating power* was also observed. Reference to the well-known atomic volume curve will show that potassium, rubidium, and caesium have the largest atomic volumes, these elements occupying the highest maxima on the curve. Salts of these elements usually crystallize from aqueous solutions without water of crystallization, and salts of these metals have been shown by direct experiment to have very little hydrating power when in aqueous solution. Lithium and sodium also occupy maxima on the atomic volume curve, but have much smaller atomic volumes than the three elements named above. Some of the salts of lithium and sodium crystallize with two and three molecules of water.

The elements cobalt, nickel, copper, manganese, iron, and chromium fall at the third minimum in the atomic volume

curve. The salts of all of these metals crystallize with large amounts of water, and all of them show in solution great hydrating power. Aluminium with about one-half the atomic weight of iron has a somewhat greater atomic volume. It lies at the second minimum on the atomic volume curve. Its salts show great hydrating power, and crystallize from solution with as much as from six to eight molecules of water.

If now we turn to the metals of the alkaline earth group, we see that barium has the largest atomic volume, and barium chloride crystallizes with two molecules of water, while the chlorides of calcium, strontium, and magnesium crystallize with six molecules of water each. The atomic volumes of magnesium, calcium, and strontium are less than the atomic volume of barium. The magnesium cation has the smallest atomic volume of any element of this group, and has the greatest hydrating power. Calcium has a smaller atomic volume than strontium and has a greater hydrating power. Strontium has a larger atomic volume than calcium, and has a smaller hydrating power.

These relations¹ can readily be seen by consulting the curve sheets already referred to.

The above described relations seem to be sufficiently general to justify the conclusion that water of crystallization is closely connected with atomic volumes, in a number of cases—the smaller the atomic volumes the larger the amounts of water of crystallization. We have seen that there is a very close relation between water of crystallization and hydrating power. There must, therefore, be a connection between the magnitude of the atomic volumes of the cations and the hydrating power of the salts, and the relation indicated by such facts as those described above is that *the hydrating power is an inverse function of the atomic volume.*

The question then arises: Why do ions with small atomic volumes have greater power to combine with water, than atoms with larger atomic volumes? It is probably connected in some way with the electrical density of the charge upon the ions—the smaller the ionic volume the greater would be

¹ J. Chim. Phys., 3, 455 (1905).

the density of the charge upon it. The effect of hydration upon the velocities of the ions was also pointed out by Jones and Pearce.¹ The velocities of the ions are a function of their mass, and perhaps of their volumes. If there were no hydration of the ions, we should, then, expect those ions with the smallest mass and smallest atomic volumes to have the greatest velocities, under a constant driving force.

We find that, with the exception of hydrogen and hydroxyl, the elements with the largest atomic volumes—potassium, rubidium, and caesium move with the greatest velocities, while the ions of the iron and copper groups, with somewhat greater masses, but with very small atomic volumes, have small migration velocities.

We have just seen that it is the cations with the smallest atomic volumes that have the greatest hydrating power. The increased mass of these ions, due to the hydrates which they carry with them, therefore causes them to move more slowly than ions with much larger atomic volumes. The existence of hydrates accounts, then, for the apparent lack of any relation between ionic velocities and the mass and size of the ions. If we take into account the hydration the apparent discrepancy disappears.

Work of Stine.

Jones and Stine² studied the effect of one salt with hydrating power upon the hydration of another salt present in the same solution. The pairs of salts with which they worked are: calcium chloride and potassium chloride; calcium chloride and magnesium chloride; calcium chloride and strontium chloride; magnesium nitrate and strontium nitrate; magnesium nitrate and calcium nitrate; aluminium chloride and ferric chloride; calcium nitrate and calcium chloride; sodium bromide and lithium bromide; and, finally, potassium chloride and ammonium chloride, which have practically no hydrating power.

The problem resolved itself into calculating the approximate composition of the hydrates formed by both of the sub-

¹ THIS JOURNAL, **38**, 737 (1907).

Ibid., **39**, 313 (1908).

stances present in the solution, and, as can be seen at a glance, was a difficult one. Indeed, the difficulties involved in calculating the approximate composition of the hydrates formed by one substance in the presence of water were multiplied many times when two substances were present.

However, by taking into account as closely as possible all of the factors involved—and they are many—we were able to throw considerable light on the problem. The effect of a salt with a common ion on the conductivity of a second salt was apportioned in terms of the law of mass action. The formula was worked out for calculating the freezing point lowering due to hydration when only one salt has hydrating power, and, similarly, the corresponding formula when both salts form hydrates.

It will be recognized that in the pairs of salts selected above we have a large variety of conditions represented. The first two have a common anion and only one has any appreciable hydrating power. Further, one salt is a binary and the other a ternary electrolyte. The next four pairs are ternary electrolytes, having a common anion, and both members of each pair have large hydrating power. The next two are quaternary electrolytes with a common anion and both have large hydrating power. The next two have a common cation. The pair next to the last have a common anion, and both members show considerable hydrating power, while the last pair have a common anion and neither member has any appreciable hydrating power.

It was found that when two hydrated salts are mixed each dehydrates the other to a certain extent, and that the magnitude of this action is conditioned by the law of mass action, which could be the case only if the composition of the hydrates as worked out was approximately correct.

It was further shown that the ions and the molecules have very different hydrating power, and that while, in general, the ions have the greater power to form hydrates, in some special cases the molecules have a greater power than the ions to combine with water.

Some interesting results were obtained with the pair of

electrolytes, potassium chloride and ammonium chloride, which have but little hydrating power. When two salts having a common ion are mixed, each drives back the conductivity of the other, and it has been thought that this is due almost entirely to each suppressing the dissociation of the other. If this were the sole explanation, then we should have the greatest effect on the conductivity under the conditions under which the salts in question were most dissociated.

Since the dissociation is greater at 0° than at 25° , for example, the effect on the conductivity ought to be greater at the former than at the latter temperature.

The fact is exactly the reverse.¹ There is very little driving back of the conductivity at 0° , considerable effect at 12° , and a very pronounced difference between the conductivity of the mixed salts and the sum of the separate conductivities at 25° .

It is thus obvious that the suppression of the ionization is not the only factor that must be taken into account here. This is especially true since a number of the solutions referred to above are practically isohydric.

The other factors that must be taken into account are:

(1) Change in viscosity of the solution on mixing the two salts.

(2) Change in the size and mass of the ionic spheres, due to a change in the hydration when the two salts are mixed.

"Thus, the effect of one salt upon another present in the same solution is not as simple as has been supposed but involves the action of several factors which have to be taken into account."

Work of Jacobson.

The work of West on the temperature coefficients of conductivity and of dissociation was continued by Jacobson.² He improved the method that had been earlier used, and extended the investigation to lithium chloride, lithium bromide, lithium nitrate, lithium sulphate, sodium nitrate, disodium phosphate, potassium sulphocyanate, potassium chromate,

¹ THIS JOURNAL, 39, 399 (1908).

² *Ibid.*, 40, 355 (1908).

potassium dichromate, calcium nitrate, strontium chloride, strontium nitrate, strontium formate, barium bromide, barium nitrate, barium formate, barium acetate, magnesium sulphate, cupric bromide, chromium chloride, chromium nitrate, ferric chloride, ferric nitrate, nickel sulphate, nickel acetate, cobalt sulphate, cobalt acetate, lead nitrate, trichloroacetic acid, racemic acid, picric acid, propionic acid, *o*-nitrobenzoic acid, and *m*-nitrobenzoic acid.

It will be seen that the compounds were so chosen as to cover as wide a range of physical and chemical properties as possible.

The increase in the conductivity of electrolytes with rise in temperature is largely due to the fact that the ions in the presence of water are hydrated. With rise in temperature the magnitude of the hydration becomes less and less, and the mass of the ions and probably their size become less. They would, consequently, move through the solvent with greater velocity and the conductivity would increase.

Those ions that are hydrated to the greatest extent would then be most affected by rise in temperature. An examination of the experimentally established facts will show that they are in accord with this conclusion.

It was shown that the conductivity of electrolytes increases with rise in temperature, *not as a linear function, but as a parabolic one*. Water, however, is an exception. Its conductivity increases with rise in temperature, as a linear function of the temperature. This is probably due to the fact that the hydrogen and hydroxyl ions from the dissociated water are not appreciably hydrated, and there is, therefore, no marked change in the hydration with rise in temperature. The increase in the conductivity of water with rise in temperature is due chiefly to the diminishing viscosity of this solvent as the temperature is raised. The change in the viscosity with rise in temperature is known to be a linear function of the temperature. Therefore, we should expect the temperature coefficient in the case of a substance like water to be a linear function of the temperature. Jacobson calls attention to the importance of hydrolytic dissociation

as affecting conductivity, and points out that many of the apparently abnormal results that have been obtained are due to this cause.

His investigation confirms, in general, the conclusions drawn by Jones from the work of West, and is, therefore, in perfect accord with the hydrate theory.

Spectroscopic Investigation of Jones and Uhler.

The spectroscopic investigation, which is the outcome of certain color changes in solution to which Dr. G. N. Lewis kindly called my attention, had for its object the study of the rôle played by hydration as conditioning certain color changes in solution with change in concentration and on the addition of a second salt. Thus, the change in the color of aqueous solutions of copper salts with change in the dilution is very well known. Further, the purplish-red color of aqueous solutions of cobalt chloride is changed to blue on the addition of a concentrated solution of calcium chloride.

"In¹ the present investigation these color changes were studied quantitatively. The absorption spectra of the substances separately, and when mixed in known quantities, have been observed by means of a direct reading spectroscope, and the wave lengths of the absorption bands read off and recorded. What is of far greater importance, however, is the photographic record of such absorption bands, and the changes in the positions of these bands as varying amounts of one or another dehydrating agent is added to the salt in question."

A grating spectrograph was used for securing the photographic records, and a direct vision spectroscope for the eye observations. The solutions were placed in cells with quartz ends to allow of work also in the ultraviolet region. A spark rich in ultraviolet light was employed and the Nernst filament was also used. The films employed were Seeds' L-ortho cut films.

The substances studied at different concentrations in water were: cobalt chloride, cupric chloride, and cupric bromide.

¹ Carnegie Publication, No. 60, p. 161 (1907).

It was found that the absorption bands widen for every salt with increase in the concentration of the solution. This leads us to say a word as to what is meant by absorption of light by dissolved substances.

In order that a substance in solution should stop a beam of light it must yield or form something in the solution that is thrown into resonance by the light. If it absorbs only certain wave lengths of light, as in the case of colored solutions, the dissolved substance must yield "absorbers" which can be thrown into resonance by those wave lengths of light which are stopped by the substance. Light waves are vibrations in the ether. In order that they may be stopped, their energy must be expended in some manner, as in throwing electrons into vibration. Absorption of light, then, means resonance.

With this idea in mind we can proceed to interpret the results obtained by Jones and Uhler.

The absorption bands widen with increase in the concentration of the solution. A widening of the absorption bands means that there is something in the solution which vibrates in resonance with a larger number of wave lengths of light. What absorber could there be in a more concentrated solution of cobalt chloride that would vibrate in resonance with a larger number of wave lengths of light than in a more dilute solution?

Jones and Uhler interpret this result as follows: We know that the hydrate present in the more concentrated solution is simpler than in the more dilute. The vibrating particle or "absorber" is, then, less loaded down and hampered in its vibrations in the more concentrated solution, and can, therefore, vibrate in resonance with a larger number of wave lengths of light. A larger number of wave lengths are accordingly cut out in the more concentrated solution and the absorption bands widen.

Jones and Uhler studied not only the effect of increasing the concentration of the solution of a single substance on its power to absorb light, but also the effect of adding a dehydrating agent in the form of a second salt to the solution of the colored salt. Thus, calcium chloride was added to

cobalt chloride, calcium bromide to cobalt chloride, aluminium chloride to cobalt chloride, calcium chloride to copper chloride, calcium bromide to copper chloride, aluminium chloride to copper chloride, calcium chloride to copper bromide, calcium bromide to copper bromide, and aluminium chloride to copper bromide.

The effect of the addition of the dehydrating agent in the form of a second salt is to *widen the absorption band*. It, therefore, produces the same effect as increasing the concentration of the colored salt alone, and can readily be explained in the same manner. The dehydrating agent removes a part of the water from the colored salt—makes the hydrate less complex. The vibrating particles, or "absorbers," are freer to vibrate in resonance with a larger number of wave lengths of light, since they are surrounded by a smaller atmosphere of the solvent. Their freer vibration enables them to cut out a larger number of light waves and, consequently, to widen the absorption bands.

The hydrate theory accounts, then, satisfactorily for the widening of the bands produced by increasing the concentration of the solution, and also by adding a second salt with a large hydrating power.

Further, it was pointed out by Jones and Uhler¹ that this is the only theory thus far proposed that does account satisfactorily for all of the facts brought out by them.

The theory of Engel, that the blue color of solutions of cobalt chloride is due to the presence of double salts, is untenable for a number of reasons. Jones and his coworkers have shown that double salts do not exist in solution to any very great extent. Further, this theory is at variance with the fact that a concentrated aqueous solution becomes blue on heating, and also with the facts established in nonaqueous solutions.

The theory of Ostwald, which would refer the blue color to the cobalt salt molecule, and the red color to the cobalt ion, is insufficient. It cannot account satisfactorily for the blue color produced on warming a concentrated aqueous

¹ Carnegie Publication, No. 60, p. 232 (1907).

solution of cobalt chloride. The dissociation would change only slightly, and hydrolysis would not liberate sufficient hydrochloric acid to drive back the dissociation appreciably.

It does not account for the fact that a very small amount of water changes to red a solution of cobalt chloride rendered blue by aluminium chloride. It fails to account for the fact that the amount of water required to turn red a blue alcoholic solution of anhydrous cobalt chloride is many times too small to produce an increased dissociation sufficient to give the observed color change.

Further, this theory is entirely incapable of explaining results obtained by Jones and Anderson¹ in their recent work on absorption in solution, and which will soon be published in full by the Carnegie Institution, of Washington, and in part in THIS JOURNAL. This work has shown that when the number of molecules in the path of the beam of light is kept constant, certain absorption bands, such as the ultraviolet absorption of copper, the red bands of cobalt salts, the ultraviolet band of cobalt chloride, and the absorption of iron chloride, *narrow with the dilution*, and there are still other facts known which the Ostwald theory cannot explain.

The theory of Dannan and Bassett, that the blue color of cobalt salts is due to complex ions of cobalt, is also insufficient. For example, it has been shown by Hartley and others that the effect on the absorption of increasing the concentration of the solution is essentially the same as that produced by a rise in temperature.

This is strong evidence against the theory of aggregates or complex ions as accounting for the color changes, since the change in the aggregates produced by *increase in concentration* is exactly the *opposite* of that produced by *rise in temperature*. It is obvious that the theory of solvation to account for the color changes is not open to this objection, since it is well known that rise in temperature produces the *same* effect on solvates as increase in concentration. The solvates become simpler with increase in concentration, and also with rise in temperature.

¹ Carnegie Publication, No. 110 (1909).

All of the facts brought out by Jones and Uhler, and also those established by Jones and Anderson, working in aqueous solutions, can be accounted for satisfactorily in terms of the hydrate theory and in terms of this alone. It now remains to see whether the facts established in nonaqueous solutions can also be accounted for in terms of the theory of solvation.

The work of Jones and Uhler was extended to solutions in nonaqueous solvents, such as methyl alcohol, ethyl alcohol, and acetone, and the salts investigated were: cobalt chloride in methyl alcohol, cobalt chloride in ethyl alcohol, cobalt chloride in acetone, copper chloride in methyl alcohol, copper chloride in ethyl alcohol, copper chloride in acetone, copper bromide in methyl alcohol, and copper bromide in ethyl alcohol. For work with these solutions in nonaqueous solvents a form of cell was devised which did away entirely with all forms of cement, since no cement could be found which would resist entirely the action of all of these solvents. The cell used by Jones and Uhler¹ worked perfectly satisfactorily.

To these nonaqueous solutions varying amounts of water were added, and the effect on the absorption bands recorded by means of photographs. The effect of the addition of water was, in every case, to *narrow the absorption band*. This is regarded as an important fact as bearing upon the hydrate theory. As more and more water was added the hydrates formed became more and more complex. The "absorbers" were, thus, more and more limited in their resonance, by the larger and larger hydrate around them, and could vibrate in resonance only with a smaller number of wave lengths of light. Consequently, the absorption bands became narrower and narrower as the amount of water present increased.

Work of Jones and Anderson on the Absorption Spectra of Solutions.

The work of Jones and Anderson, on absorption spectra in nonaqueous solutions, also established a number of facts

¹ Carnegie Publication, No. 60, p. 242 (1907).

which are of importance as bearing on the hydrate theory. This is especially true in the case of neodymium chloride in methyl alcohol, for example, and in mixtures of methyl alcohol and water. When the amount of water present is only a few per cent, we have *two distinct spectra*, one corresponding to the aqueous solution, and the other to the nonaqueous solution. These two spectra appear simultaneously, the one or the other being more intense depending upon the relative amounts of water and the alcohol present. This seems to be the first time that such an observation has been made. A number of other points bearing upon the hydrate theory were brought out in the work of Jones and Anderson, but as a pretty full account of this work will soon be published in THIS JOURNAL, no further details will be given here.

To summarize, then, the evidence that has been obtained thus far, as bearing upon the solvate theory, we have:

(1) The relation between water of crystallization and lowering of the freezing point, holding for such a large number of substances, is regarded as strong evidence for the existence of complex hydrates in aqueous solutions.

(2) The fact that the minimum in the boiling point curve for a given substance occurs at a greater concentration than the minimum in its freezing point curve is just what would have been predicted from the solvate theory.

(3) The relation between water of crystallization and temperature of crystallization—the lower the temperature the larger the amount of water of crystallization—is strictly in accord with what would be expected from the solvate theory.

(4) The connection between the hydrating power of the ions and the temperature coefficients of conductivity is a strong argument in favor of the solvate theory. Those ions with the greatest hydrating power have the largest temperature coefficients, as we would expect; and the more dilute solutions containing more complex hydrates have larger temperature coefficients than the more concentrated.

(5) The evidence for the existence of solvates in nonaqueous

solvents is of the same general character as that for the existence of hydrates in aqueous solutions.

(6) The existence of a pronounced conductivity maximum in certain mixed solvents shows that the ions are surrounded by an atmosphere of the solvent, which changes in magnitude with change in the composition of the mixture.

(7) The fact that dissociation as measured by the freezing point method is greater than as measured by conductivity was predicted from the solvate theory before a single comparative measurement was made. It was also shown in this work that the smaller ions have the greater hydrating power.

(8) The effect of one salt with hydrating power upon another salt present in the same solution, also having hydrating power, was predicted by the hydrate theory, and is in conformity with the law of mass action.

(9) The evidence for the solvate theory, from the study of the absorption spectra of aqueous solutions, is certainly most striking. The absorption bands widen with the concentration, due to the hydrate becoming simpler, and the "absorbers" being freer to vibrate. They also widen with the addition of a dehydrating agent, and for the same reason.

(10) The absorption spectra in nonaqueous solutions to which more and more water is added furnish evidence, which is equally strong, for the existence of hydrates. With addition of water to the nonaqueous solution its absorption bands grow narrower, due to the hydrates around the absorbers becoming more and more complex.

Further spectroscopic evidence for the existence of hydrates in aqueous solutions, and of solvates in solution in general, will be furnished when the work of Jones and Anderson, and also that of Jones and Strong, are published.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
October, 1908.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXV.—RESEARCHES ON PYRIMIDINES:
ON THE FORMATION OF PURINE DERIVATIVES FROM
4-METHYLCYTOSINE.

[FORTY-FIRST PAPER.]

BY CARL O. JOHNS.

It was found by Gabriel and Colman that 4-methyl-6-aminopyrimidine¹ and 2-chlor-4-methyl-6-aminopyrimidine² did not give the expected 5-nitro compounds when nitrated, but instead yielded 6-nitramine derivatives.

When 4-methylcytosine, I.,³ is nitrated in the presence of sulphuric acid, an almost quantitative yield of 4-methyl-5-nitrocytosine, II., is obtained. To determine whether the compound formed was a 6-nitramine or a 5-nitropyrimidine, the nitration product was heated with 30 per cent sulphuric acid in a sealed tube. This treatment gave Behrend's nitromethyluracil,⁴ III., in which the nitro group occupies position 5. This result agrees with previous observations made when pyrimidines containing an amino group in position 6 have been heated with sulphuric acid. When cytosine⁵ was heated with 20 per cent sulphuric acid it gave uracil, and when nitrocytosine⁶ was heated under similar conditions, nitrouracil was formed.

The reduction of 4-methyl-5-nitrocytosine to 2-oxy-4-methyl-5,6-diaminopyrimidine, IV., presented considerable difficulty. This was not unexpected since it was only after many unsuccessful attempts that 2-oxy-5,6-diaminopyrimidine⁷ was obtained by the reduction of 5-nitrocytosine.

An attempt to reduce 4-methyl-5-nitrocytosine with stannous chloride did not give the desired diaminopyrimidine, and when ammonium sulphide was used, 4-methylcytosine

¹ Ber. d. chem. Ges., **34**, 1240 (1901).

² *Ibid.*, **34**, 1241 (1901).

³ THIS JOURNAL, **40**, 348 (1908).

⁴ Ann. Chem. (Liebig), **240**, 3 (1887).

⁵ Wheeler and Johnson: THIS JOURNAL, **29**, 494 (1903).

⁶ Johnson, Johns, and Heyl: *Ibid.*, **38**, 116 (1906).

⁷ *Ibid.*, **38**, 170 (1906).

was regenerated. The reduction was finally accomplished by the use of aluminium amalgam. Even then prolonged reduction or a temperature above 45° liberated ammonia and regenerated 4-methylcytosine. If the solution which was obtained from the reduction was evaporated on a water bath at 100° a black residue was obtained. The evaporation was therefore carried out under diminished pressure. When the solution had been concentrated to a small volume, stout, flat crystals of the 2-oxy-4-methyl-5,6-diaminopyrimidine separated. These contained one and one-half molecules of water of crystallization. They could be recrystallized from water without undergoing decomposition and then separated in long prisms that contained but one molecule of water. It is probable that the decomposition observed when the solution obtained from the reduction was evaporated was due to the presence of some unstable by-product.

Gabriel and Colman condensed urea¹ and thiourea² with 4-methyl-5,6-diaminopyrimidine and obtained purine derivatives.

The writer has found that 2-oxy-4-methyl-5,6-diaminopyrimidine also condenses with urea and thiourea to give 2,8-dioxy-6-methylpurine, V., and 2-oxy-6-methyl-8-thiopurine, VI. Moreover, formic acid acts on 2-oxy-4-methyl-5,6-diaminopyrimidine and produces a monoformyl derivative. This compound gives a sodium salt which loses water, when heated, and yields 2-oxy-6-methylpurine, VII.

These reactions with urea and formic acid are such as might be expected of an orthodiamine but not of a hydrazine derivative, and they confirm the assumption that 4-methylcytosine nitrates in position 5.

Emil Fischer³ has called attention to the fact that the introduction of oxygen into purine decreases its solubility in water. In accordance with this, 2-oxy-6-methylpurine is easily soluble in hot water while the same purine with oxygen or sulphur in position 8 is almost insoluble.

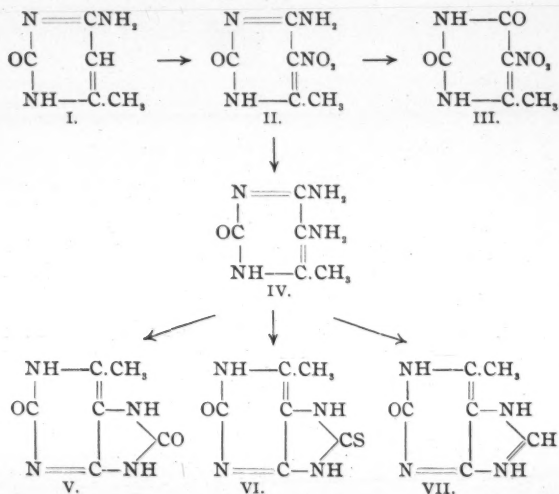
If 2-oxy-5,6-diaminopyrimidine were heated with urea it

¹ Ber. d. chem. Ges., **34**, 1247 (1901).

² *Ibid.*, **34**, 1248 (1901).

³ Untersuchungen in der Puringruppe, p. 74.

might be expected to yield 2,8-dioxypurine. This compound is the only one of the three possible dioxypurines which has not been prepared and it has the structure which was at first assigned to xanthine. Later, Emil Fischer showed that xanthine was 2,6-dioxypurine.¹ 6,8-Dioxypurine has been prepared by Fischer and Ach.² The writer has begun work on the synthesis of 2,8-dioxypurine.



EXPERIMENTAL PART.

$$\begin{array}{c} \text{N}=\text{CNH}_2 \\ | \\ \text{OC} \quad \text{CNO}_2 \\ | \quad || \\ \text{NH}-\text{C}\cdot\text{CH}_3 \end{array}$$

4-Methyl-5-nitrocytosine, —Four grams of 4-methylcytosine were dissolved in 11 cc. of concentrated sulphuric acid. Heat was liberated. While the solution was still

¹ Ber. d. chem. Ges., 30, 553 (1897).

² Ibid., 30, 2218 (1897).

warm 11 cc. of nitric acid, density 1.5, were added gradually. The first portions of nitric acid produced considerable heat but no red fumes were evolved. The resulting solution was allowed to stand at room temperature for 10 minutes and was then poured into 100 cc. of cold water. When the acids were neutralized with ammonium hydroxide, 4.8 grams of a yellow precipitate, which corresponds to 90 per cent of the calculated yield, separated. This compound was difficultly soluble in boiling water and crystallized in small pointed prisms. Its slight solubility in water showed that it was not 4-methylcytosine. It began to turn brown at 260° and became black at 280° but did not melt. It was soluble in acids and ammonia.

Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_4$.	Found.
N	32.94	33.17

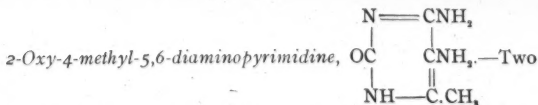
The position of the nitro group was determined as follows: One gram of the nitro compound was dissolved in 20 cc. of 30 per cent sulphuric acid and heated in a sealed tube at 130°–140° for two hours. A deposit of large crystals was obtained when the tube cooled. These were filtered off and the filtrate was analyzed for nitrogen in the form of ammonia by adding sodium hydroxide and distilling into N/10 hydrochloric acid.

N calculated for one NH_2 group, 0.08 gram.

Found, 0.09 gram.

The crystals which were filtered off dissolved readily in boiling water and separated from the cold solution in stout prisms and toothed structures. They possessed all the properties of Behrend's nitromethyluracil, in which the nitro group occupies position 5.

	Calculated for $C_5H_5O_2N_3$.	Found.
N	24.56	24.99



and two-tenths grams of finely pulverized 4-methyl-5-nitro-

cytosine were suspended in 100 cc. of water and reduced vigorously with 1 gram of aluminium amalgam for one-half hour. The temperature was kept below 45° . The aluminium used was in the form of fine drillings. The aluminium hydroxide formed was filtered off by suction and washed with hot water. The filtrate was concentrated under diminished pressure to about 15 cc. Crystals separated during the evaporation. These were redissolved by careful heating and a slight insoluble residue was filtered off. Stout, flat prisms separated on cooling. These became brown above 250° and decomposed slowly at about 280° – 285° without melting. They contained one and one-half molecules of water of crystallization. The yield of pure hydrous crystals was from 50 to 60 per cent of the calculated. Water determinations on crystals obtained from different experiments gave the following results:

- I. 1.6340 gram lost 0.2637 gram of H_2O .
 II. 0.5011 gram lost 0.0805 gram of H_2O .
 III. 1.1859 gram lost 0.1907 gram of H_2O .

	Calculated for $C_5H_5ON_4 \cdot 1\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	16.16	16.14	16.06	16.08

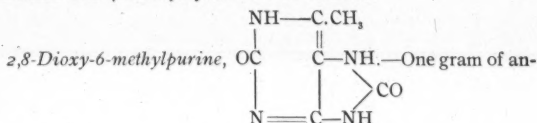
Nitrogen determinations resulted as follows:

	Calculated for $C_5H_5ON_4 \cdot 1\frac{1}{2}H_2O$.	Found.
N	33.53	33.61
	Calculated for $C_5H_5ON_4$.	Found.
N	40.00	39.78

When the flat crystals obtained above were recrystallized from water they separated in long prisms that contained but one molecule of water of crystallization. The following analyses were made on different lots of the recrystallized diaminopyrimidine.

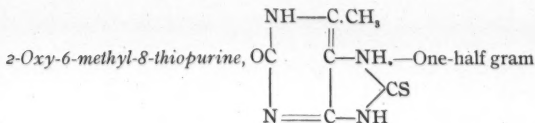
	Calculated for $C_5H_5ON_4 \cdot H_2O$.	I.	Found. II.	III.
H_2O	11.39	11.53	11.49	11.42
	Calculated for $C_5H_5ON_4$.			Found.
N	40.00			40.02

2-Oxy-4-methyl-5,6-diaminopyrimidine was easily soluble in hot water but it dissolved only slightly in cold water. It did not dissolve in alcohol. The dried crystals were very hygroscopic. Water solutions gave precipitates with mercuric chloride and picric acid. The picrate charred above 240° but did not melt. The best yield was obtained by using fine aluminium drillings and reducing rapidly. If the reduction is prolonged or the temperature raised above 45° , ammonia is liberated and 4-methylcytosine is re-formed.



hydrous 2-oxy-4-methyl-5,6-diaminopyrimidine was intimately mixed with 1 gram of urea by grinding in a mortar. This mixture was heated in an oil bath kept at 170° – 180° for one-half hour. The mass melted and ammonia was evolved. The fusion product was dissolved in boiling water containing a few drops of ammonium hydroxide and the solution was decolorized with animal charcoal. When the filtrate was boiled to drive off ammonia, minute crystals separated. These were almost insoluble in boiling water but dissolved readily in mineral acids and bases. They were insoluble in alcohol or acetic acid. They did not melt at 345° . The yield was 1.1 grams, or 93 per cent of the calculated weight.

	Calculated for $C_5H_6O_2N_4$	I.	Found.	II.
N	33.73	33.59		33.81



of 2-oxy-4-methyl-5,6-diaminopyrimidine was ground in a mortar with one gram of thiourea. The mixture was heated in an oil bath kept at 180° – 190° for one hour. It melted and

turned black. Ammonia was evolved. The fusion mass was dissolved in water containing ammonium hydroxide. A clear solution was obtained by using animal charcoal. This solution gave an immediate precipitate when acidified with acetic acid. The compound thus obtained was purified by dissolving in very dilute ammonium hydroxide and reprecipitating with acetic acid. Extremely small crystals were obtained. These were not soluble in alcohol and were almost insoluble in boiling water and boiling acetic acid. They were freely soluble in alkalies and mineral acids. They did not melt at 345° . The yield of the pure purine was 80 per cent of the calculated quantity.

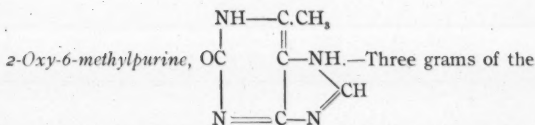
	Calculated for $C_5H_5ON_4S$.	Found.
N	30.77	30.90
S	17.59	17.81

The Monoformyl Derivative of 2-Oxy-4-methyl-5,6-diaminopyrimidine, $C_5H_7ON_4CHO$.—Four grams of the diaminopyrimidine were dissolved in 4 cc. of formic acid, density 1.2, and the solution was heated on a water bath for one-half hour. The excess of formic acid was evaporated in an open dish and the residue was dissolved in water. When this solution was neutralized with ammonium hydroxide, the monoformyl derivative precipitated. It was moderately soluble in hot water and formed minute crystals when the solution was cooled. It dissolved readily in acetic acid and was slightly soluble in boiling alcohol. The crystals began to turn black at about 325° but did not melt at 345° .

	Calculated for $C_5H_7O_2N_4$	Found.
N	33.33	33.29

Prolonged heating in an oil bath at 240° caused the formyl derivative to darken considerably but it did not lose water to form a purine. When recrystallized from water the heated product exhibited all the properties of the formyl derivative. It was dried at 130° for analysis.

	Calculated for $C_5H_5O_2N_4$	Found.
N	33.33	33.46



monoformyl derivative of 2-oxy-4-methyl-5,6-diaminopyrimidine were dissolved in an excess of 10 per cent solution of sodium hydroxide. When alcohol was added the sodium salt of the formylpyrimidine separated as a white powder. This salt was dried and heated in an oil bath at 200° . Water came off readily and considerable foaming ensued, leaving a porous crust. This dissolved freely in cold water and did not give a precipitate when the solution was neutralized with acetic acid. The solution was therefore evaporated to dryness and the residue was dissolved in a little hot water. Clusters of slender prisms were obtained when the solution cooled slowly. These turned brown at about 280° and became black above 300° but did not melt at 345° . They were easily soluble in acetic acid and ammonium hydroxide and sparingly soluble in boiling alcohol. A water solution gave a precipitate with mercuric chloride but did not give precipitates with ferric chloride, copper sulphate, or chloroplatinic acid.

	Calculated for $C_6H_6ON_4$	I.	Found. II.	III.
N	37.33	37.05	37.10	37.35

NEW HAVEN, CONN.,
November, 1908.

OBITUARY.

WOLCOTT GIBBS.

Probably the oldest and certainly one of the most distinguished chemists of the United States died December 9th at his home, Newport, R. I., Wolcott Gibbs was born in New York City, February 21, 1822. He received his early education at the grammar school attached to Columbia College, and then graduated from the college in 1841. He evidently had a bent towards chemistry in his early life, for after graduating from college he spent a few months in the laboratory of Dr. Robert Hare, in Philadelphia. He then returned to New

York and studied medicine, receiving the degree of doctor of medicine from the College of Physicians and Surgeons in 1845. He spent a year and a half working in the laboratories of Rammelsberg and Heinrich Rose in Berlin. He was for some time at Giessen under Liebig, and then attended Regnault's lectures on physics at the College of France. On returning to the United States, in 1848, he gave a short course of lectures at Delaware College. From 1849 to 1863 he was professor of physics and chemistry at the College of the City of New York, when he was elected to the Rumford professorship in Harvard College and was placed in charge of the laboratory of the Lawrence Scientific School. This position he held for 24 years. Since then he has been professor emeritus, living at Newport, R. I.

He was one of the original members of the National Academy of Sciences, and from 1885 to 1891 was its president. He was a foreign member of the London Chemical Society and an honorary member of the German Chemical Society.

Most of his original work has appeared in the "Contributions to Chemistry from the Lawrence Scientific School," and he has published elaborate memoirs on the platinum metals, on the ammonia-cobalt bases, on new analytical methods, and on complex inorganic acids, discovering platino-tungstates, vanadio-tungstates, vanadio-molybdates, etc. In physics he has published papers on wave lengths of light, on vapor densities, improved methods of gas analysis, and on the theory of the dynamo. Of recent years his articles have appeared chiefly in the *American Journal of Science* and in *THIS JOURNAL*.

Throughout his long life Dr. Gibbs was true to the highest scientific ideals and his influence on scientific research in this country was most beneficial. When he began his work he was almost alone so far as chemistry is concerned. It was a great pleasure to him that as time went on the number of those who devoted themselves to research increased more and more. His interest in all advances was great and did not diminish until within a few years. Long after he had passed his seventieth birthday he planned new researches and showed almost youthful enthusiasm on learning of some brilliant discovery.

REPORTS.

THE ORIGIN OF PETROLEUM.¹

Owing to the confusion existing in the minds of many from a lack of understanding of the great number of experimental facts and theories regarding the origin of petroleum which have accumulated during the past twenty years, it is necessary in discussing this subject to consider its historical development. In addition to the cosmic theory, according to which the oil has condensed upon our planet from interplanetary space, there are the two important theories, known as the inorganic and organic, which have been suggested to explain the origin of the oil. The father of the inorganic theory is A. von Humboldt. This investigator concluded, on the basis of the proximity of certain hot springs and oil wells in South America, that the oil was the product of a destructive distillation of the older rocks. Berthelot, in 1866, was the first to offer a chemical explanation of its formation. According to this author the alkali metals and carbon dioxide reacted, forming metallic acetylides which, in turn, acting with water vapor at high temperatures, formed acetylene and oil. In 1877 Mendeléeff, and at about the same time Cloez, explained its formation as due to the action of water on hot metallic carbides in the interior of the earth. Moissan accepted this theory, as did also, on the basis of their classical work on this subject, Sabatier, and his coworkers, Senderens and Mailhe. Sabatier and Senderens established the following facts:

(1) When acetylene and an excess of hydrogen are passed over nickel, cobalt, or iron at moderate temperatures, methane and an oillike substance, consisting mainly of marsh gas hydrocarbons, resembling in general properties the Pennsylvania petroleum, is obtained.

(2) When the same action takes place at 200° the hydrocarbons first formed combine with more hydrogen and form an oil resembling the Caucasian oil and containing marsh gas hydrocarbons and naphthenes.

(3) If the product obtained in (1) is passed, with an excess of hydrogen, over nickel at 300°, an oil resembling the Galician oil, containing unsaturated cyclic hydrocarbons, is formed.

(4) By the action of nickel on a mixture of acetylene and

¹ Report of a lecture delivered by C. Engler at Jena, May 11, 1908, and published in *Z. ang. Chem.*, **21**, 1585.

an insufficient supply of hydrogen an oil is obtained which stands between the Pennsylvania and Caucasian oils.

From these results the following conclusions were drawn regarding the formation of oil:

Water acting upon the free metals and carbides gives hydrogen and acetylene, and these gases, in contact with nickel or other metals, condense to form petroleum, the variety depending upon the conditions under which the condensation takes place. This inorganic theory of the origin of petroleum is, however, not tenable because it cannot give a satisfactory explanation of the presence of nitrogenous bases and especially because most natural petroleum shows optical activity, a phenomenon which, in the light of known facts, is not in accord with an inactive source; for while this is not theoretically impossible, yet in the study of synthetical processes the formation of optically active compounds from inactive materials has not been noted.

While, previous to the knowledge of the presence of nitrogenous bases and of the optical properties of oil, many chemists supported the Mendeléeff hypothesis, some chemists and all the geologists, and especially Hoefer, accepted only the organic theory to explain its origin.

If the theory of the animal origin of oil was accepted it was still necessary to explain how oil containing very little or no nitrogenous materials could be formed from substances rich in this element, for an oil rich in nitrogenous materials was obtained by the distillation of fish. These observations and the known facts as to the great stability of the fats and waxes led to the suggestion by the author that the formation of oil from animal materials takes place in two stages, the first consisting in the destruction and removal of the nitrogenous compounds and nonfatty materials by fermentation processes, and the second in the conversion of the fatty residue into oil. In the formation from plants in a similar way the cellulose and related substances are first destroyed, leaving the fats and waxes, which later are changed into oil. This theory found confirmation in the work of Krämer, who found in some animal remains from sea mud, which had partly undergone decomposition, 20 per cent of fat when the normal amount in the live animal was 15.7 per cent; and in the work of Goedicke, who found that the fat content of a partly decomposed organism, whose normal amount in the living stage was 10 per cent, had risen to 18 per cent. It is of great interest and importance also that the author was able, in 1888, to obtain an almost quantitative yield of an oil having the general proper-

ties of petroleum by the distillation, under pressure, of fish, animal or plant fats, and even of synthetical glycerides and fatty acids.

This evidence produced a marked change of allegiance, on the part of chemists, from the inorganic to the organic theory. Soon, however, a new discussion arose as to whether the oil, acknowledged to be of organic origin, was formed from animal or vegetable materials. In considering the "vegetable hypothesis" it is necessary to make a distinction between the old view, according to which the oil was derived from the large plants of the uplands and from the carbon formed from these, and the more recent view, supported by Krämer, according to which the oil is formed from water and marsh plants, such as diatoms and algae. The weight of chemical and geological evidence is against the former; but as the possibility of the other theory is not denied, the statement is generally made that it is derived from both animal and vegetable sources. As a source of animal origin the macrofauna need not be considered as the most important, for Witt has called attention to the fact that the microfauna of the seas and shallow waters is also a very important source. The objection has been made to this theory that if the oil has an animal origin it should, on account of the immense amount of animal life in the seas, occur in much larger quantity; but just as in each age only a small proportion of the vegetable material was converted into coal, so only a small part of the fauna of each age may have been changed into bitumen and finally into oil. In describing the source of oil the term "fatty materials" must be used in the broadest way and understood as including liquid fats, waxes, rosin, balsam, cholesterol, tannic acid, and other substances of the same general nature. The nitrogenous matter is mostly destroyed and removed by fermentation processes and the carbohydrates must also be removed to a large extent, for the carbon formed from these is not found in the oil nor in the neighborhood of oil deposits. That the carbohydrates, however, do take some part in the formation of oil by first being changed to fats by the action of microorganisms has been established, and it makes no difference, from a chemical standpoint, whether this change is produced by microorganisms, macroorganisms, or foraminifera. In every case the nearest source is fat. Many of the objections to the author's theory are based on misconceptions. For instance, the objection has been made that the temperature (350° - 400°) at which the experiments were generally carried out would in the natural process, on the

basis of an increase of 1°C . for every 33 meters, demand too great a depth at which the oil must have been formed. One author has calculated this depth to be 30,000 feet. Results obtained by a number of independent investigators have been uniformly lower than this value, the results obtained varying from 5. to 13.7 meters for each degree of temperature. The variations in the composition of oils is probably due to variations in temperature and pressure at the time of formation. In addition to the pressure due to the superimposed horizontal layers, a marked lateral pressure may be caused by faults, upheavals, etc., and produce a marked increase in temperature. Scheithauer found that where brown coal was subjected to a pressure of 1200-1500 atmospheres the temperature of the mass rose 80° to 100° .

Wepfer calculated that the pressure in the Alps due to faults was about 1720 times the compressive strength of granite, which is 1000 atmospheres per cm. The raising of mountain ranges or the depression of the floor of the sea would produce not only an enormous lateral pressure and an elevation of temperature, but in many cases a relative change in the position of the layers. The observation that oil is found along great mountain ranges is in harmony with these facts, and the occurrence of oil in deep layers in level country is not irreconcilable with them. In discussing the temperature necessary to produce the oil from plants and animals it should not be forgotten that time and temperature may compensate one another and that a change that is produced in a short time at a high temperature may be produced at a lower temperature in a long time.

The geologist and chemist regard the change of organic material into oil from different points of view. For example Potonié, a geologist, distinguished between the process leading to the formation of oil from water flora and fauna and the process by which land and swamp plants are converted into coal, while a chemist demands the exact mechanism of the changes and justly expects an answer. These questions can be answered in the following manner: The *first stage* of the changes into bitumen consists in a fermentation reaction during which the albumen and the cell substance of the plant disappear to a considerable extent. Only the fats, waxes, some fatty acids, and a small amount of other materials remain. In the *second stage* the saponification of the glycerides with the formation of free fatty acids is effected by the action of water or by fermentation, or both, and the esters of the waxes are also hydrolyzed. The residues in many oils are

probably due to incomplete decomposition. In a *third stage* the acids or esters decompose with formation of carbon dioxide, and the alcohols, oxalic acid, etc., with formation of water, leaving a residue consisting of complex hydrocarbons and some oxygen compounds. These substances have been regarded by some investigators as intermediate products. Next follows in a general way the formation of the liquid hydrocarbon mixtures of the oils by a violent reaction which causes the splitting up of the complex intermediate products with the formation of gaseous products. In these reactions a long continued low temperature could have produced the same results as a high temperature for a short time and it has been proved experimentally that the method of decomposition of complex fats and carbohydrates can be controlled by making changes in the temperature and pressure. The last change must have taken place at a high temperature and at a great depth, otherwise during the long time which has passed since these substances were formed the gases resulting from the decomposition of the complex compounds would have escaped. Thorpe and Young and others have shown that paraffin formed from saturated hydrocarbons gives, when decomposed under pressure, unsaturated hydrocarbons, so the presence of such compounds in oils can be readily explained. In the course of time and under the influence of a fluctuating temperature these unsaturated compounds form polymerization and addition products of high molecular weights and less liquid in nature, thus making another stage in the building up process of the oil. The author has found experimentally that such changes do take place, as there is a constant change in the specific gravity and other properties of the artificially prepared oils.

The hydrocarbon groups that would be represented according to this explanation of their formation would be as follows:

1. Members of the marsh gas series are formed directly by the decomposition of the "bitumen," this substance consisting of the product formed by the loss of carbon dioxide from the fatty residues and containing hydrocarbons of high molecular weights and some free fatty acids and esters.
2. Members of the ethylene series must be formed, for the complex saturated hydrocarbons would, by decomposition, give a simpler saturated compound and an unsaturated compound, thus: $C_{2n}H_{4n+2} = C_nH_{2n+2} + C_nH_{2n}$. On account of the unsaturated nature of these compounds and of their strong power of forming polymeric and addition products, or else due to the changes produced by distillation, these hydrocarbons would, in course of time, disappear.

3. It is highly probable that the large amount of naphthene present in some varieties of oil has been formed by the decomposition by heat and under pressure of certain aromatic acids or esters or of a number of other compounds. The view held by the author and by Krämer that the naphthene might be formed also by the action of heat and pressure on the primary olefine has been experimentally confirmed by Aschar who obtained a hexanaphthene and higher homologues by the action of aluminium chloride on amylene. The author then confirmed this result by subjecting an olefine to a high temperature in a sealed tube for some days.

4. The lubricating oil is a mixture of saturated and unsaturated hydrocarbons of a number of series. This could have been formed in three ways and perhaps all of these may have played a part in its formation. It may have been formed by direct decomposition of the fatty residue, for Engler and Singer found experimentally that an oil of this kind was formed in a case where fish blubber was distilled under pressure. Of greater importance, however, is the method which depends upon the self polymerization and addition of the unsaturated compounds formed by the decomposition of the organic residues, for these substances, in their unsaturated condition, could not remain separate if in close contact. The author, unlike LeBel and Heusler, does not consider that catalysis is necessary to produce this change, for he has found that the unsaturated compounds, by the action of heat and pressure, pass over into high boiling, viscous oils when only a small amount of aluminium chloride is present. A synthesis by Krämer and Spilher supports the view held by the author.

5. Benzene and its homologues, which are found in different oils in widely differing amounts, could have been formed by the decomposition of the fatty material at a moderate temperature. The author and Lehmann, by the distillation of blubber, obtained benzene, toluene, *m*-xylene, pseudocumene, and mesitylene. In the natural process of oil formation this action must take place at 300°-400°. Albumens and phenylacetic ester both form benzene hydrocarbons. The author does not consider the view, held by Bertels, Radziszewsky, and others, that petroleum was formed exclusively by fermentation processes, to be tenable. While bacteria and enzymes play a very important part in many transformations it is not a safe conclusion, so far as oil is concerned, that this has been the only force at work.

Evidence presented by G. Meyer, who found petroleum in certain deposits formed by bacterial action, and C. B. Morrey,

who found fossil bacteria in oil-bearing rocks, are considered by the author as of little weight, as they are either not yet conclusively proved or can be readily explained on his theory. No direct evidence has been found for this view, while against it is the experimental observation that when cinnamic acid is treated with *Penicillium glaucum* or *Aspergillus niger* the product formed is almost entirely marsh gas and never oil-like hydrocarbons, with the exception of traces of styrene. The fact that high temperatures are not favorable to bacterial action and that the soil acts as a bacterial filter would be against the possibility of the formation of oil by such action in the lower deposits and at high temperatures. There is in fact an overwhelming mass of evidence in favor of the view that it is only in the first part of the process that fermentation plays any part.

The Origin of the Optically Active Constituents.—The activity must be due to the presence of an active residue of the original strongly active source or of the residue of the activity produced in the formation of the substance, as optically active opposites generally form an inactive substance. Walden based his view of the vegetable origin of petroleum on the ground that the oil, like many active vegetable materials and especially a fossil vegetable material, showed nearly always righthanded activity. The author says that the activity of the original substance and the derivatives is not always the same, that there are many righthanded animal derivatives, and that the plantlike fossil upon which the view was largely based was probably not derived from fat, but from rosin.

Neuberg suggested albumen as the source of the active constituents of petroleum; but the substances formed by its decomposition are chiefly products of low molecular weights, while the active constituents of oil are high molecular compounds. Neuberg pointed out, however, that from an optically active fatty acid and a high molecular inactive fatty material an active oil could be obtained. The author at first considered the activity of the oil to be due chiefly to admixture with a single substance, but later found that in a great number of cases, where the boiling temperature, under diminished pressure, of the active fraction was being studied, the activity increased to a maximum and then decreased as the temperature was raised. In most cases this maximum point occurs with the portion boiling between 200°–300°. In some cases two maxima were observed with inactive portions lying between. In a sample of oil from Java the lower boiling portions were laevorotatory, then followed an inactive portion,

which was followed in turn by a dextrorotatory oil. These reactions can be best explained by the assumption that the activity is due to *cholesterin*. A number of investigators have studied this problem and while some have pointed out the similarity of the product obtained from *cholesterin* with the oil, others have found that the products formed by the distillation of *cholesterin* are dependent upon the way in which the distillation is conducted. For example, when this substance was heated for one hour to 350° the product was strongly dextrorotatory, while when heated to 300° no marked change from the laevorotatory condition could be noticed. Between 300° - 350° in the course of one hour the marked change from the laevo to the dextro condition occurred. Phytosterin behaved in a similar way to the *cholesterin*.

The results obtained by Albrecht in an investigation of the optically active portion of Galician oil showed that only a very small amount of *cholesterin* need be present to explain the activity of the oil. In the formation of oil the amount of *cholesterin* destroyed was small as compared with the amounts of fatty and waxlike residues lost, thus causing a natural concentration of the active constituents. Neuberg's objection to this explanation that the organic materials in the earth are not rich enough in *cholesterin* to account for the amount necessary has been rendered untenable by the discovery by Marcusson of rich sources of this substance in nature. As further proof that *cholesterin* is the cause of the activity the author cites the great similarity in the behavior of an artificial oil made up of inactive components and *cholesterin* to that of the natural oils, and also the similarity of Java oil to the *cholesterin* distillate, the dextro and laevorotatory substances being obtained not only in the same order but at the same temperature in the two materials. Still stronger confirmation was furnished by the experiments of the author and Lederer. As before mentioned, with *cholesterin* the laevo distillate on heating becomes a dextrorotatory substance. The laevorotatory portion of Java oil is derived from the *cholesterin*; but does not become dextrorotatory when heated. If it is sealed in a tube and heated it does change to the dextro variety. Unless this process is very carefully carried out the dextro variety, by racemizing or by some other method, is destroyed. Moreover, that the optically inactive portion is really made up of equally strong dextro and laevo components is shown by the fact that by the same process as described above this inactive portion becomes dextrorotatory, owing to the change of the

laevo portion to the dextro variety. These observations suggest the possibility of the inactive oils being racemic varieties of the two active varieties and that all optically active oils in the course of time, or more quickly when heated, pass over by one of several possible methods into an inactive form, thus making the active oils transition products not completely changed. The author closes by acknowledging that perhaps some oil may have been formed from inorganic source; but he believes that the main supply is of organic origin, vegetable or animal, or both.

J. E. G.

PREPARATION OF SALTPETER BY THE PROCESS OF THE BADISCHE ANILIN- UND SODA-FABRIK.¹

To meet the ever-increasing demand for nitrogenous fertilizers, three sources of nitrogen are available: (1) Ammonia formed in the preparation of coke and gas by the distillation of coal; (2) the Chile saltpeter beds; and (3) the inexhaustible supply of nitrogen in the air. As the ammonia obtained from coal is merely a by-product, and the saltpeter beds are rapidly nearing exhaustion, the problem of the fixation of atmospheric nitrogen is becoming more and more important, and several methods by which this can be accomplished have been successfully worked out. Of these, two are now familiar to every one: first, the cyanamide process, based on the absorption of nitrogen by heated calcium carbide, with formation of calcium cyanamide; and secondly, the Birkeland-Eyde process for the manufacture of nitrates. It has been known since the time of Priestley and Cavendish that when electric sparks are passed through moist air the nitrogen combines with the oxygen, and nitric acid is formed. According to our present views, this reaction is a purely thermal one and is in no way due to any specific property of electrical energy. As in all endothermic reactions, *i. e.*, such as are accompanied by absorption of heat, the higher the temperature the greater the amount of reaction product, in this case nitric oxide, which is formed. Thus, for example, at 3000°, 4.5 per cent, by volume, of nitric oxide can be obtained from air, but at 1800° only 0.7 per cent is formed. The reaction is reversible, and not only does the velocity of formation of the nitric oxide increase with the temperature, but the reverse dissociation into nitrogen and oxygen does also. In order, therefore, to obtain the maximum possible amount of nitric oxide, the mixture of oxygen and nitrogen must first be heated to a high temperature

¹ Report on a lecture delivered by Dr. O. Schönherr at the general meeting of the Verein deutscher Chemiker at Jena, June 11, 1908, and published in *Z. angew. Chem.* **21**, 1633.

and then suddenly cooled to avoid loss through the dissociation of the nitric oxide. In the Birkeland-Eyde process this object is attained by forcing the air at right angles through an electric arc so deflected by powerful magnets as to offer as large a surface as possible. The process of the Badische Anilin- und Soda-Fabrik is based on the same principle, but instead of being forced through the flame, the air is carried along a quietly burning arc of great length. The apparatus used consists essentially of a tube whose end is connected to one pole of the machine furnishing the current, while at the other end of the tube, but isolated from it, is placed an electrode connected to the other pole of the machine. The arc is now lighted, usually by making the distance between the electrode and the wall of the tube sufficiently small, and the air is forced in at a tangent so that it passes through the tube with a spiral or whirlwind motion. It carries along one end of the arc before it until it reaches the end of the tube, when the arc continues to burn quietly in the center of the tube while the air rapidly whirls around it. In this way arcs 5 meters long are produced and burn quietly for weeks at a time without relighting. The company has now three furnaces, with a total of about 2000 horse-power, in operation in Christianssand in southern Norway. The furnaces are very durable, the only part which suffers rapid deterioration being the lower electrode which either consists simply of iron rods or may be constructed of conductors of the second class, such as zircon oxide. In this process there is less waste of electrical energy and the nitrogen oxides are obtained in greater concentration than in all other known processes. The Badische Anilin- und Soda-Fabrik has combined with the owners of the Birkeland-Eyde process for the manufacture of nitrates, and plants having an aggregate of 120,000 horse power are in course of construction in Norway. C. A. R.

REVIEWS.

THE CHEMISTRY OF THE DIAZO-COMPOUNDS. By JOHN CANNELL CAIN, D. Sc. (Manchester and Tübingen); Editor of the Publications of the Chemical Society; Joint Author of "The Synthetic Dyestuffs and the Intermediate Products from which They are derived." London: Edwin Arnold. 1908. pp. x + 172.

Chemists will find this small book an excellent guide to the study of the diazo-compounds. The author says: "I have endeavored to describe our present knowledge of the Diazo-compounds and to give an account of the enormous progress made in this important branch of Organic Chemistry since Griess's epoch-making discovery just fifty years ago."

The literature of the subject is very confusing but the author has evidently studied the original articles carefully and dealt with the material in a fair-minded way. Referring to the principal causes of the confusion he says: "I have striven to give an exact account of the long controversy between Hantzsch and Bamberger on the constitution of the diazo-compounds. The most important contributions to the literature have hitherto been made by Hantzsch (*Die Diazoverbindungen*, Ahrens' Sammlung, 1902) and his former pupil, Eibner (*Zur Geschichte der aromatischen Diazoverbindungen*, Oldenbourg, 1903), so that the opposite view has, perhaps, not been set forth quite so fully, although the admirable Report to the British Association by Morgan (*Our Present Knowledge of Aromatic Diazo-compounds*, 1902) leaves nothing to be desired."

Full references to the literature are given and apparently this part of the work has been done conscientiously. The book is warmly recommended to teachers and students.

I. R.

SYNTHETISCH-ORGANISCHE CHEMIE DER NEUZEIT. VON DR. JULIUS SCHMIDT, A. O. Professor an der Königl. Technischen Hochschule Stuttgart. Braunschweig: Vieweg und Sohn. 1908. Seiten x + 185. Preis: geheftet, M. 5.50; geb. in Leinwand, M. 6.20.

The ground covered by this excellent treatise can best be indicated by giving the titles of the different chapters.

Chapter I. Importance of the organomagnesium halides for synthetic purposes.

Chapter II. Some synthetic results in the sugar group. Asymmetric synthesis.

Chapter III. Synthetic reactions which give aldehydes and ketones.

Chapter IV. Dimethyl sulphate as a methylating agent.

Chapter V. Syntheses by means of azides.

Chapter VI. E. Fischer's methods for the synthesis of polypeptides.

Chapter VII. Syntheses by the splitting off and transformation of cyclic bases.

Chapter VIII. Syntheses in the field of the alkaloids, of artificial medicinal agents, and in the purine group.

Chapter IX. Syntheses of dyes and of polynuclear aromatic compounds.

Chapter X. Syntheses of perfumes, of hydroaromatic and related compounds.

Chapter XI. Electrolytic syntheses of various organic compounds.

No synthetic reaction has ever found such rapid and extensive application as that which we owe to Grignard. It is, however, surprising to learn that in the period of eight years more than 450 articles have appeared that have to deal with the application of organic magnesium compounds of the type R. Mg. Hlg to synthetic purposes.

Regarding the influence of the introduction of synthetic indigo in the production of natural indigo we learn that in 1902 the production in Bengal had fallen off 48 per cent. In 1902 the quantity of natural indigo, estimated as 100 per cent indigo blue, amounted to 3 millions of kilograms while the quantity of the artificial indigo was 5 millions of kilograms. The price of pure indigo blue which, before the introduction of the artificial product, was from 16 to 20 marks a kilogram fell towards the end of 1905 to 7 to 8 marks.

The artificial preparation of camphor has long been the subject of investigation. It is stated that a Berlin firm has recently put upon the market considerable quantities of this product. All methods for its preparation that are of practical interest start with pinene. The importance of the problem involved is shown by the following statement of A. Hempel: "The world's consumption of camphor is calculated at 3 to 4 millions of kilograms per year, of which 1 million falls to Germany. * * * * At present the price of camphor is 1000 marks for 100 kilograms. In spite of this known actual valuation the Japanese monopoly furnishes the principal consumers, the celluloid manufacturers and refiners, crude camphor containing 90 per cent at 450 marks.

"It may confidently be assumed that Japan will meet competition by low price as soon as the artificial product is put upon the market. The prices may then fall to the level reached in 1898, perhaps below 200 marks."

The book is interesting and valuable.

I. R.

THE CHEMICAL BASIS OF PHARMACOLOGY. An introduction to Pharmacodynamics based on the Study of the Carbon Compounds. By FRANCIS FRANCIS and J. M. FORTESCUE-BRICKDALE. London: Edward Arnold. 1908. pp. 372. Price, \$4.

The correlation of pharmacological action with the structure of chemical compounds has long proved an attractive field of investigation for both pharmacologist and chemist, but it must be confessed that the generalizations which it has been possible to formulate as a result of studies of this nature have seldom proved capable of wide application. This is due in part to insufficient experimental results but also to lack of coöperation between the chemist and pharmacologist. The

present volume is of special interest owing to the fact that one of the authors (Professor Francis) is well known for his researches in pure organic chemistry, while the other author is primarily a clinician. It must be admitted, however, that despite certain admirable sections, the book as a whole is disappointing.

The arrangement of the material commencing with the chapters dealing with general chemical and physiological principles, followed by sections on the fatty and aromatic hydroxy compounds and their derivatives, and lastly those dealing with the more complicated nitrogen-containing substances, leaves little to be desired. An interesting account is given of the various urethane and urea derivatives which possess marked hypnotic properties and some of which are actually employed in practical therapeutics. Of these the product introduced by Emil Fischer and von Mering, known as "Veronal" (diethylbarbituric acid), appears to be the most important. It is stated to surpass in intensity of action all the hypnotics hitherto employed and the cost of an effective dose is less than that of any other hypnotic except chloral hydrate.

The later chapters deal with the alkaloids, glucosides, and synthetic substitutes for cocaine, atropine, etc., and the book closes with a section in which the dependence of taste and odor upon chemical structure is discussed.

It is surprising to find adrenalin placed under the heading of "Substitutes for Hydrastis," as is also the statement that the extract prepared from suprarenal glands, which contain the adrenalin, is "the most important body *recently* introduced into medicine." As a matter of fact the extract has been in common use for about ten years and the crystalline active principle was obtained by Takamine and Aldrich in this country in 1901.

The work might have been greatly improved by adequate proof-reading and by more careful reference to the original sources of information. It is perhaps due to the authors to give specific examples of these inaccuracies. Taking a few consecutive pages at random one finds for example on p. 68 that β -oxypropylaldehyde is converted by oxidation into β -oxybutyric acid and on the same page the formulae for butyric aldehyde and butyric acid are incorrectly given. On the following page the statement concerning the fate of formic acid in the body is misleading, while the information on page 73 as to the combustion of oxalic acid in the tissues contains no reference to recent work. On page 72 the substance C_2H_5 .

HSO_4 is incorrectly named, while on page 75 the statement implying the absence of sulphocyanide excretion following acetonitrile administration is incorrect, as is also the statement, on the same page, that only two benzene derivatives are present in the protein molecule, no account being taken of tryptophane (indoleaminopropionic acid). The assertion that α -phenylpropionic acid gives rise to homogentisic acid in cases of alcaptonuria is also without basis in fact. An account is given on page 77 of Knoop's investigations of the mechanism of animal oxidation which omits the more important observations, and the statement that phenyl fatty acids, other than phenylpropionic acid, with more than two carbon atoms in the side chain do not yield benzoic acid is incorrect, since Knoop's crucial experiment upon which the theory of β oxidation is largely based consisted in the observation of the excretion of benzoic acid (hippuric acid) after administration of phenylvaleric acid.

Enough has been written to show that the book requires a large amount of careful revision before it can hope to attain any great measure of success.

H. D. DAKIN.

ELEMENTS OF WATER BACTERIOLOGY, WITH SPECIAL REFERENCE TO SANITARY WATER ANALYSIS. By SAMUEL CATE PRESCOTT and CHARLES EDWARD AMORY WINSLOW. Second edition, rewritten. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1908. pp. xii + 258. Price, \$1.50.

The first edition of Prescott and Winslow's little book on Water Bacteriology has proved an exceedingly useful guide to workers in this field, representing, as it did, the consensus of opinion of the best American bacteriologists. We are therefore especially glad to see a second edition considerably larger and more comprehensive than the first. In addition to a new chapter on the Bacteriology of Sewage and Sewage Effluents, several chapters have been rewritten and brought up to date, namely, those dealing with methods of isolation of typhoid bacillus, the presumptive tests for *B. coli* and the significance of intestinal bacteria, other than *B. coli*, in suspected water.

The present edition may be most cordially recommended to students.

W. W. FORD.

THERMOELEMENTE UND THERMOSÄULEN. Ihre Herstellung und Anwendung. Von PROFESSOR DR. FRANZ PETERS, Dozent an der Königlichen Bergakademie zu Berlin. Mit 192 in den Text gedruckten Abbildungen. Halle a. S.: Verlag von Wilhelm Knapp. 1908. pp. 180.

This number of the "Monographien über angewandte Elektrochemie" brings together in a convenient and scientific

form what is known in reference to thermoelements. It is probably the most satisfactory treatise on this subject that has ever been written and since it includes what was published even in the first half of the year 1907 it is fully up-to-date.

The section dealing with the various chemical elements used in making thermoelements is the most interesting reading. The following metals are mentioned as electrodes: aluminium, antimony alloys, metals of the cerium and chromium groups, iron, copper, nickel, and nickel alloys, platinum, silicon, tellurium, bismuth, zinc. Copper sulphide, lead sulphide, carbon, etc., are also used.

This monograph seems to be of the same high standard as the other volumes of this series.

H. C. J.

DIE CHEMISCHE AFFINITÄT UND IHRE MESSUNG. Von DR. OTTO SACKUR, Privatdozent an der Universität Breslau. Mit fünf Abbildungen im Text. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1908. pp. 129.

This interesting and important monograph is one of "Die Wissenschaft" series. The problems dealt with are those which lie right at the basis of chemical science. As the author states in his preface, chemists have recognized the importance of thermodynamics for chemistry ever since Van't Hoff pointed out that the measure of the chemical forces manifested between reacting substances is the maximum work which the transformation in question can do. Sackur expresses his indebtedness for the thermodynamic developments to Nernst, Blanck, and Haber. "I hope," says he, "that I have succeeded in presenting clearly the great advance which chemistry owes to thermodynamic methods of dealing with chemical problems, and thus have furthered its general recognition;" and a careful study of this monograph will show that this hope has been realized.

The subject is treated in six chapters. The first is a historical development of the conception of chemical affinity. The second deals with the principle of maximum work and the second law of thermodynamics. The third chapter has to do with the calculation of affinity from the amount of the transformation; the fourth with the electrical method of measuring affinity; the fifth with affinity and temperature; and the sixth and last chapter gives some results of the measurement of affinity—results from reactions between compounds, and from reactions between the elements.

With the exception of the first and last chapters the monograph is literally filled with differential equations, and this suggests a thought which has doubtless occurred to every

teacher of advanced chemistry. That is, the desirability, indeed, the absolute necessity of a good elementary knowledge of the so-called higher mathematics, in dealing with the fundamental problems of chemical sciences.

It is still true that one can learn much about the empirical facts of chemistry without a knowledge even of the calculus, just as one can learn something about the empirical facts of physics without any extended knowledge of mathematics. But as no one can even approach the fundamental principles underlying the science of physics without a good knowledge at least of differential equations, so, also, is it impossible to master the fundamental principles underlying chemistry as a science without an elementary knowledge of thermodynamics.

It is difficult to overestimate the importance of impressing these facts upon students of chemistry who are just beginning their careers.

H. C. J.

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